İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SELF-CURABLE POLYESTER BY REACTION OF GLYCIDOL WITH MALEIC ANHYDRIDE

M.Sc. Thesis by
Bünyamin Karagöz

Department : **Polymer Science and Technology**

Programme: **Polymer Science and Technology**

MAY 2003

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Date of submission: 23 June 2003
Date of defence examination: 26 May 2003

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Prof.Dr. Tuncer ERCİYES

MAY 2003

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

GLİSİDOL VE MALEİK ANHİDRİT'İN REAKSİYONU İLE KENDİ KENDİNE SERTLEŞEBİLEN POLİESTER ELDE EDİLMESİ

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Tezin Enstitüye Verildiği Tarih : 23 Haziran 2003
Tezin Savunulduğu Tarih : 26 Mayıs2003

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MAYIS 2003

ACKNOWLEDGEMENT

This master study has been carried out at Istanbul Technical University, Chemistry Department of the Science & Letter Faculty.

First of all, I would like to express my gratitude to my supervisor Prof.Dr. Niyazi Bıçak and Assoc.Prof. B.Filiz Şenkal for sharing their deep knowledge, experience and continuous encouragement throughout my research.

I also would like to thank to my colleagues Fevzi Çakmak Cebeci, Mustafa Gazi, Emine Kazancıoğlu,Abdullah Aydoğan, Erdem Yavuz and Argun Gölçeören for their helpful attitude during my laboratory works.

Finally, I would like to dedicate this thesis to my parents Kadir and Gülbahar KARAGÖZ, my brother Zekeriya KARAGÖZ. I owe much to my family for all their self-sacrifice, patience and support during all my education.

May 2003 Bünyamin Karagöz

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LIST OF SYMBOLS

M.A	:	Maleic Anhydride
G.L	:	Glycidol
MeOH	:	Metanol
MeCN	:	Acetonitrile
$COCl_2$	:	Phosgen
H_2SO_4	:	Sulfuric acid
BF_3-Et_2O	:	Boron triflouride etherate
HMPA	:	Hexametylphosphor amide
HCl	:	Hydrochloric acid
DMF	:	Dimethyformamide
THF	:	Tetrahydrofurane
NaOH	:	Sodium hydroxide
$\mathbf{M_n}$	:	Number average molecular weight
$\mathbf{M_w}$	:	Weight average molecular weight
[η]	:	Intrinsic viscosity

SELF-CURABLE POLYESTER BY REACTION OF GLYCIDOL WITH MALEIC ANHYDRIDE

SUMMARY

Maleic anhydride is unique compound in preparing unsaturated polyesters.Presence of maleate (unsaturated) groups in polyesters inparts dyereseption and postcrosslinkable abilities. Although apriciable percentage of maleate units isomerized to fumarate units during the process this isomerization does not increase processing time in hardening by copolymerization with styrene. Copolymerization with styrene is most common way of hardening polyesters.In fact this is one of the most tedious step of polyester process.

In this study we have targeted to prepare unsaturated polyesters with hydroxy groups has been concluded that the hydroxy groups involved would be come reactive sites in cross-linking in another words the OH groups are expected to serve cross-linking through the maleate double bonds at elevated temperatures.

This study is confined to the reaction of maleic anhdride with glycidol.At first glance this reaction seems to be quite straightforward, by contrast the reaction may resulty in a rapid crosslinking. Indeed when the reaction is performed without solvent crosslinking occurs. Crosslinking can be avoided by controlled reaction in a aprotic solvent. We have demonstrated that soluble polyester of maleic anhydride with glycidol can be obtained by controlled processing. Such a control was achieved by step-wise heating (at 80^0 and 120^0C) of the equemolar mixtures of the monomers in dimetoxyethane.

The resulting unsaturated polyester with hydroxyl groups can be crosslinked by direct heating at 190^0C, without using additinal comonomer. In the study optimum reaction vconditions have been investigated by using DSC, and structure of the polyester has been elusidated by common spectroscobic techniques such as NMR and FT-IR .

GLİSİDOL VE MALEİK ANHİDRİT'İN REAKSİYONU İLE KENDİ KENDİNE SERTLEŞEBİLEN POLİESTER ELDE EDİLMESİ

ÖZET

Maleik anhidrit doymamış poliesterler oluşturmak için eşsiz bir bileşiktir. Poliesterlerde (maleat) doymamış gruplarının bulunması boya tutuculuk ve sonradan çapraz bağlanabilme sağlar. Reaksiyon esnasında maleat ünitelerinin önemli bir kısmı fumerata dönüştüğü halde bu stirenle kopolimerleşme yoluyla yapılan sertleştirme süresini arttırmaz. Poliesterlerin sertleştirilmesinde stirenle kopolimerleştirme sertleştirmenin en güzel yoludur.Gerçekte bu poliester işlenmesindeki en zahmetli işlerden birisidir.

Bu çalışmada hidroksil grupları içeren doymamış poliesterleri oluşturmak hedeflenmiştir. Burada hidroksil gruplarının çapraz bağlanmada reaktif merkezler olacağı düşünülmüştür.Bir başka deyişle OH gruplarının maleat grupları üzerinden yüksek sıcaklıklarda çapraz bağlanma işlevi görmesi beklenmiştir.

Bu çalışma maleik anhidrit ile glisidolün reaksiyonuyla sınırlandırılmıştır. İlk bakışta bu reaksiyon çok kolay yürüyecekmiş gibi gözükmektüdir. Ancak bunun aksine hızlı çapraz bağlanmayla sonuçlanabilir. Gerçektende çözücüsüz gerçekleştirildiğinde çapraz bağlanma olmaktadır. Çapraz bağlanma aprotik bir çözücüde kontrollü bir reaksiyonla çapraz bağlanmadan kaçınılabilir. Bu çalışmada maleik anhidrit ile glisidolün çözünür poliesteri kontrollü bir işlemle elde edilebilir olduğu gösterilmiştir. Kontrol monomerlerinin dimetoksiethandaki ekimolar karışımlarının 80^0 ve 120^0C kademeli olarak ısıtılmasıyla sağlanmıştır. Görülmüştür ki hidroksil grupları taşıyan bu doymamış poliester ilave bir komonomere gereksinim olmaksızın 190^0C' de doğrudan doğruya ısıtılmakla çapraz bağlanabilmektedir.

Çalışmada poliesterleşmenin obtimum şartları diferansiyel taramalı kalorimetre ile belirlenmiş ve poliester ürünün yapısı IR ve NMR gibi bilinen spektroskopik yöntemlerle aydınlatılmıştır.

1. INTRODUCTION

Maleic anhydride (MA) is one of the most important compounds in preparing unsaturated polyesters. Presence of maleic ester segments in copolyesters provides dye reception and post-cross-linking abilities. High electron deficiency of maleic anhydride makes it capable of charge transfer interaction. Although maleic anhydride itself is a non-homopolymerizable monomer, it forms alternating copolymers with other vinyl monomers, such as styrene [1] and vinyl acetate [2], due to its charge transfer forming ability. Similarly, maleate ester segments in unsaturated polyesters can be copolymerized with styrene monomer to give crosslinked polymers. This reaction has a widespread application for hardening of polyesters [3, 4]. Polyesters obtained from maleic anhydride or maleic acid contains both maleate or fumarate double bonds due to isomerization of maleic acid semiesters during the polycondensation at elevated temperatures [5]. Since the fumarate double bond, has a much greater reactivity in copolymerization with vinyl monomers, unsaturated polyesters with high fumarate contents undergo rapid cross-linking with styrene [6].

The double bond of maleate ester, on the other hand has remarkable reactivity towards nucleophylic addition of NH, SH or OH groups. Acid catalyzed addition of hydroxyl groups to the double bonds causes to formation of branching points with ether linkages [7], in polyesterification conditions.

Reaction of bis-epoxy compounds with dicarboxy acids to give linear polyester has been described in earlier literatures [8]. This reaction has been employed for preparing polyesters with hydroxyl groups. This approach has also been applied for cross-linking of hiper-branched polyacids [9]. An interesting method related with polyester formation is reaction of epoxy group with cyclic anhydrides [10, 11]. The reaction proceeds without water elimination and takes place in mild conditions in the presence of tertiary amine catalysts.

This study is aimed at preparing linear polyesters by reaction of maleic anhydride with glycidol. The anhydride component is expected to react first, whereas epoxy group of the glycidol must react at higher temperatures. If the reaction proceeds step by step, in this way, linear polyester with hydroxyl pendant groups can be prepared. The hydroxyl group resulting would be beneficial to impart some hydrophylicity to the polyester.

Since additional hydroxyl group forms by ring opening of the epoxy function, glycidol can be considered as a potential three-hydroxyl compound. Hence, reaction of glycidol with maleic anhydride is reminiscent of polycondensation of a trihydric alcohol with a dicarboxylic acid yielding network polyesters. Possibility of linear polyester formation, in such case must depend not only on temperature profile and stochiometry but also on reactivity differences between epoxy and hydroxyl groups in ester formation.

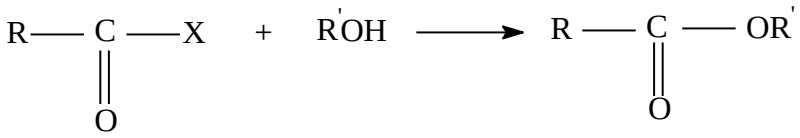
In this work, we have targeted to prepare soluble polyester from maleic anhydride and glycidol. The resulting polyester has been characterized by ^{1}H-NMR, and GPC (gel permeation chromatography). Moreover, cross-linking ability of the soluble polyester by thermal curing and cross-linking copolymerization with styrene has been studied.

2. THEORITICAL PART

2.1. Synthesis of Esters

Esters are polar compounds but lacking hydrogen attached to oxygen, their molecular can not form strong hydrogen bonds to each other. As a result, esters have boiling points that are lower than those acids and alcohols of comparable molecular weight.

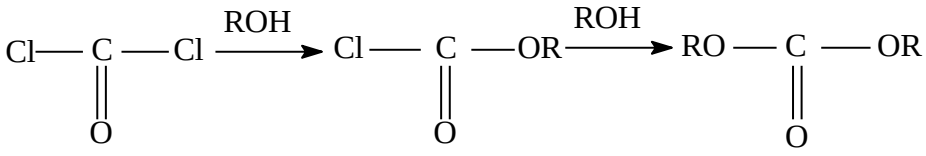
2.1.1. Alcoholysis of Acyl Halides



(2.1)

The reaction between acyl halides and alcohols or phenols is the best general method for the preparation of carboxylic esters. The reaction is of wide scope, and many functional groups do not interfere. A base is frequently added to combine with the HX formed. When aqueous alkali is used, this is called the Schotten-Baumann procedure, but pyridine is also frequently used. Both R and R' may be primary, secondary, or tertiary alkyl or aryl.

When phosgene is the acyl halide, haloformic esters or carbonates can be obtained.



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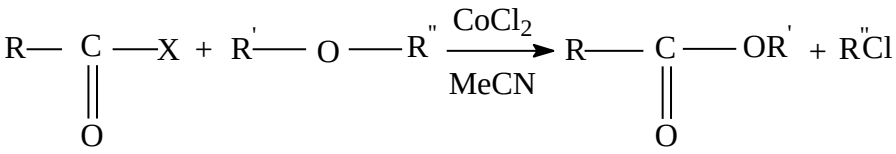
Acyl halides can also be converted to carboxylic acids by using ethers instead of alcohols, in MeCN in the presence of certain catalysts such as cobalt (II) chloride [12].



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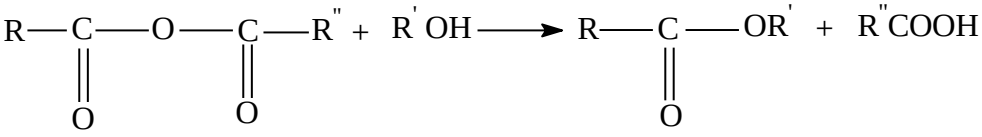
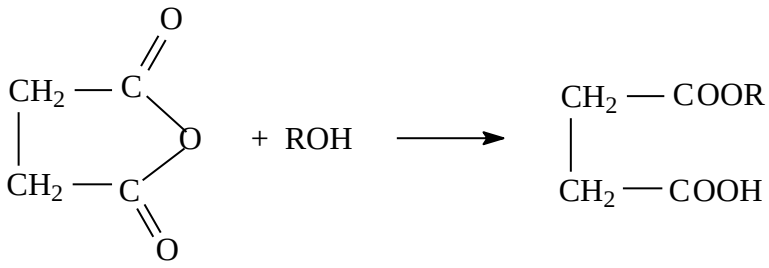
2.1.2. Alcoholysis of Anhydrides



(2.2)

Anhydrides are somewhat less reactive than acyl halides; they are often used to prepare carboxylic esters. Acids, Lewis acids, and bases are often as catalysts-most often, pyridine. Catalysis by pyridine is of the nucleophilic type. 4-(N, N-Dimetylamino) pyridine is a better catalyst than pyridine and can be used in cases where pyridine fails [13]. A non-basic catalyst is cobalt (II) chloride [14]. Formic anhydride is not stable compound but esters of formic acid can be prepared by treating alcohols or phenols with acetic-formic anhydride. Cyclic anhydrides give monoesterified dicarboxylic acids, for example



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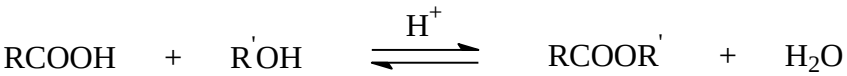
2.1.3. Esterification of Carboxylic Acids

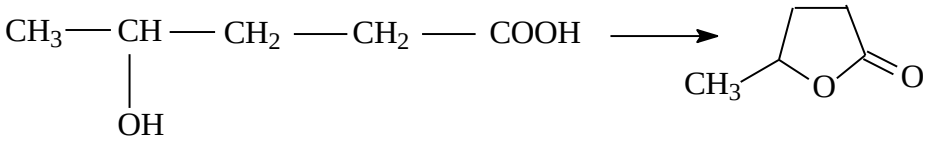


(2.6)

The esterification of carboxylic acids with alcohols [15] can be accomplished only if a means is available to drive the equilibrium to the right. There are many ways of doing this, among which are: 1- addition of an excess of one of the reactants usually the alcohols; 2- removal of the ester or the water by distillation; 3- removal of water by azeotropic distillation; and 4- removal of water by use of dehydrating agent or

molecular sieve. When $R^{'}$ is methyl, the most common way of driving the equilibrium is by adding excess MeOH; When $R^{'}$ is ethyl, it is preferable to remove water by azeotropic distillation [16]. The most common catalysts are H_2SO_4 and TsOH, though some reactive acids (formic e.g.) do not require a catalyst. Besides methyl and ethyl, $R^{'}$ may be other primary or secondary alkyl groups, but tertiary alcohols usually give carbocations and elimination. Phenols can sometimes be used to prepare phenolic esters, but yields are generally very low.

γ- and δ-hydroxyl acids are easily lactonized by treatment with acids, or often simply on standing, but larger and smaller lactones rings cannot be made in this manner, because polyester formation occurs more readily [17].



(2.7)

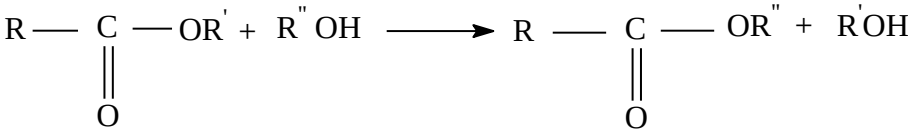
Often the conversion of a group such as keto or halogen, γ and δ to a carboxyl group, to a hydroxyl group gives the lactones directly, since hydroxyl acid cyclized too rapidly for isolation.

Carboxylic acids can be also prepared t-butyl ether by treating carboxylic acids with t-butyl ethers and acid catalysts [18].

(2.8)

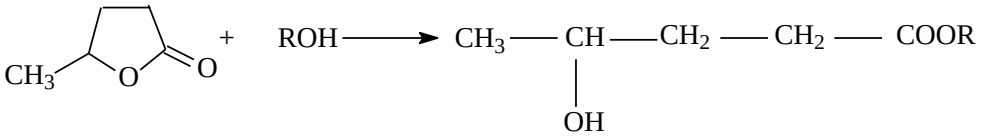
Carboxylic acids can be converted to t-butyl esters by treatment with t-butyl 2, 2, 2-trichloroacetimidate and BF_3-Et_2O.

2.1.4. Alcoholysis of Carboxylic Esters, Transesterification



(2.9)

Transesterification is catalyzed by acids or bases [19]. It is an equilibrium reaction and must be shifted in the desired reaction. In many cases low-boiling esters can be converted to higher-boiling ones by the distillation of the lower-boiling alcohol as fast as it is formed. This reaction has been used as a method for the acylation of a primary OH in the presence of a secondary OH; the diol is treated with ethyl acetate in the presence of Woelm neutral alumina [20]. Regioselectivity has also been accomplished by using enzymes (lipases) as catalysts. Lactones are easily opened by treatment with alcohols to give open-chain hydroxyl esters;

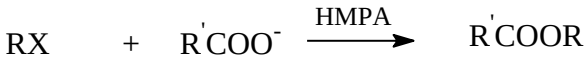


(2.10)

Transesterification has been carried out with phase-transfer catalysis, without an added solvent [21]. In other procedure, RCOOR$^{'}$ are converted to RCOOR$^{''}$ by treatment of the ester and alcohol R$^{''}$OH with *n*-BuLi, which converts the R$^{''}$OH to R$^{''}$OLi.

2.1.5 Alkylation of carboxylic acid salts

Sodium salts of carboxylic acids, including hindered acids as mesitoic, rapid react with primary and secondary bromides and iodides at room temperature in the dipolar

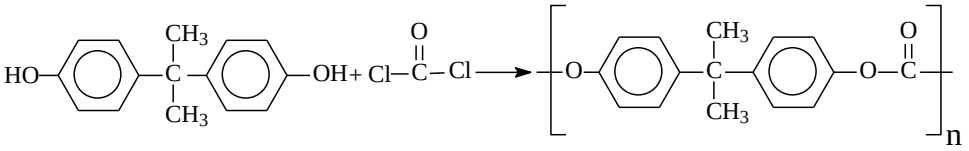


(2.11)

aprotic solvents, especially HMPA, to give high yields of carboxylic esters [22]. The mechanism is SN^2. Another method uses phase transfer catalysis. With this method good yields of esters have been obtain from primary, secondary, benzylic, allylic, and phenacyl halides.

2.1.6 Carbonate Esters

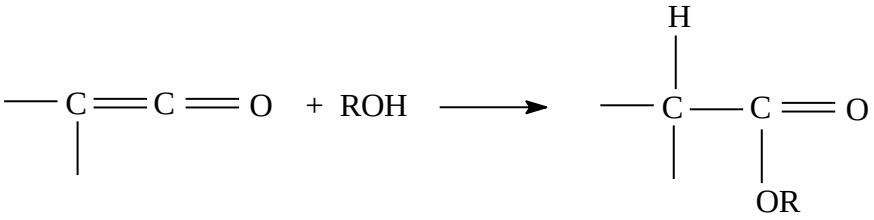
Carbonate esters can not be obtained by direct esterification of carboxylic acids instead they can be prepared from phosgene which is acid halides of the carbonic acids the well known example of this reaction is the reaction of bis-phenol-A [23].



(2.12)

2.1.7. Addition of Alcohols to Ketene

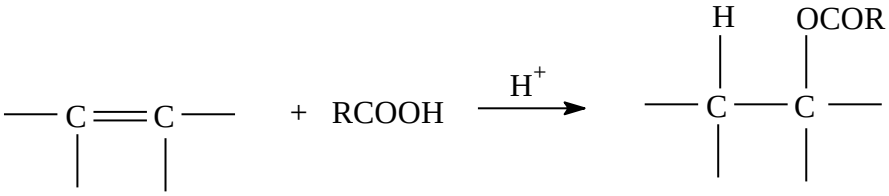
Both alcohols and phenols add to ketones to give carboxylic esters [24]:



(2.13)

This has been done intra molecularly (with the ketene and of the molecule generated and used in situ) to form medium- and large-ring lactones.

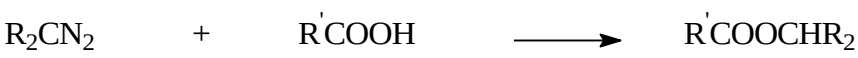
2.1.8. Addition of Carboxylic Acids to Alkenes



(2.14)

Carboxylic esters are produced by the addition of carboxylic acids to olefins, a reaction that is usually acid-catalyzed (by Lewis acids). Since Markovnikov's rule is followed, hard-to-get esters of tertiary alcohols can be prepared from olefins of the form $R_2C=CHR$. When carboxylic acids that contains a double bond in the chain is treated with a strong acid, the addition occurs internally and the product is a γ- and/or δ-lactones, regardless of the original position of the double bond in a chain, since strong acids catalyze double bond shifts [25]. The double bond always migrates to a position favorable for the reaction, whether this has to be toward or away from the carboxyl group.

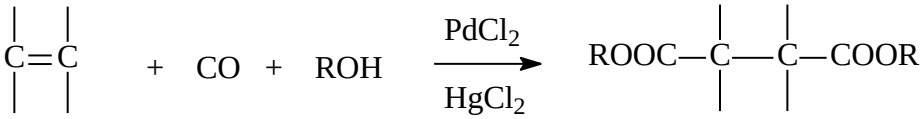
2.1.9. Alkylation of Carboxylic acids with Diazo Compounds



$$R_2CN_2 + R'COOH \longrightarrow R'COOCHR_2 \qquad (2.15)$$

Carboxylic acids can be converted to esters with diazo compounds by this reaction. In contrast to alcohols, carboxylic acids undergo the reaction quite well at room temperature, since the reactivity of the reagent increases with acidity. The reaction is used very high yields are important or where the acid is sensitive to high temperatures [26].

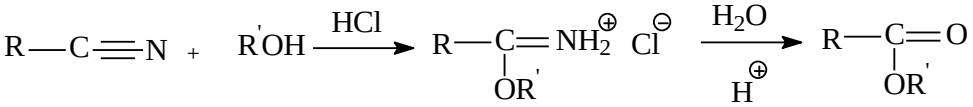
2.1.10. Dicarboxylation of Olefins and Acetylenes:



$$\text{C=C} + CO + ROH \xrightarrow[HgCl_2]{PdCl_2} ROOC\text{—C—C—}COOR \qquad (2.16)$$

Alkenes can be converted to succinic esters by reaction with carbon monoxide, an alcohol, and palladium chloride in the presence of mercuric chloride [27].

2.1.11. Alcoholysis of Nitriles

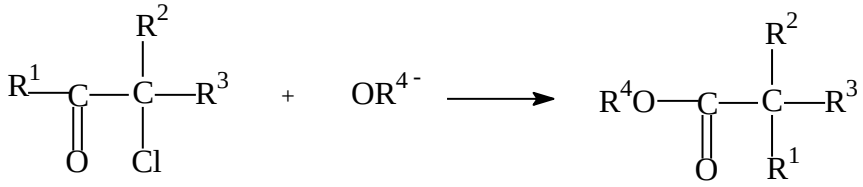


$$R\text{—C}\equiv N + R'OH \xrightarrow{HCl} R\text{—C(OR')=}NH_2^{\oplus}\ Cl^{\ominus} \xrightarrow[H^{\oplus}]{H_2O} R\text{—C(OR')=O} \qquad (2.17)$$

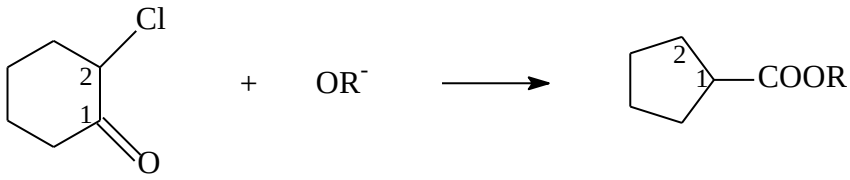
The addition of dry HCl to a mixture of a nitrile and alcohol in the absence of water leads to the hydrochloride salt of an imino ester. This reaction is called the Pinner synthesis [28]. The salt can be hydrolyzed with water and acid catalyst to the corresponding ester.

2.1.12. The Favorskii Rearrangement

The reaction of α-halo ketones (chloro, bromo, or iodo) with alkoxide ions. To give rearranged esters is called the Favorskii rearrangement. The use of hydroxyide ions or amines as bases leads to the free carboxylic acids (salts) [29] or amide, respectively, instead of the ester, Cyclic α-halo ketones give ring contraction;



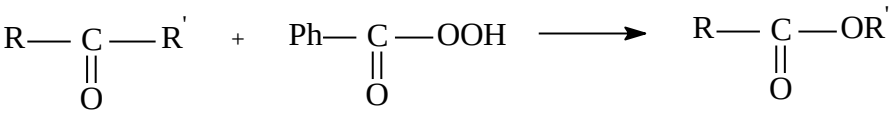
(2.18)



(2.19)

The reaction has been also carried out on α-hydroxy ketones and on α,β-epoxy ketones [30].

2.1.13. The Baeyer-Villiger Rearrangement

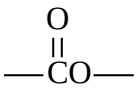


(2.20)

The treatment of ketones with peracids such as perbenzoic or peracetic acid, or with other peroxy compounds in the presence of acid catalysts, gives carboxylic esters by "insertion" of oxygen. The reaction is called the Baeyer-Villiger rearrangement [31].

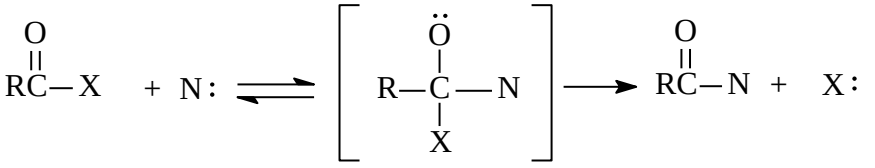
2.2 Polyesters

Polyesters are polymers with repeating carboxylate groups in their backbone chain.



(2.21)

Polyesters are synthesized by the typical esterification reactions, which can be generalized by the equation (2.22)



(2.22)

Where N: is a nucleophilic reagent such as $-OR^{1}$. The rate of the reaction will be dependent on the structure of R, R^{1}, X, N and on the whether a catalyst is used. Carothers extended much of the earlier work and helped to clarify the understanding of the polyesterification reaction in the light of the knowledge of polymer chemistry at that time.

Polyesters are heterochain macromolecular substance characterized by the presence of carboxylate ester groups in the repeating units of their main chains. The first approach yield AB-type products having a undirectional orientation of carboxylate ester groups in the molecular chain; the second leads to AA/BB-type polymer with polymers with the ester groups recurring alternately in their oxycarbonyl and carbonyloxy forms. In the homopolyesters the carboxylate ester groups are spaced regularly along the chains, but in copolyesters their separations may vary with the nature of the intervening skeletal group.

2.2.1 Polyester Properties

The properties of polyesters are determined by the proportion of carboxylate ester groups in their structure and by the geometry, polarity, and segmental mobility of their repeating units. Since their intermolecular interactions are not especially strong, the properties of polyesters are more sensitive to variations in structure than are those of strongly interacting polymers such as polyamides or polyurethanes, and hence span a wider range than for these more polar materials.

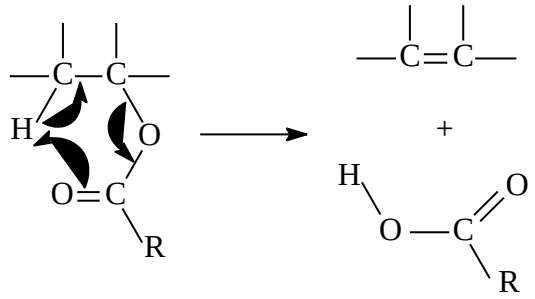
2.2.1.1 Linear Acyclic Polyesters

Polyesters of types malonate polyesters and polyglycolide with values of x and $y \geq 2$ are colorless crystalline solids with crystal melting temperatures (Tm) mostly within the rather narrow range of 40-90°C, glass-transition temperatures (Tg) - 70 to - 30°C, and densities 0.9-1.3 g/cm^{3}. At low molecular weights (>5000).

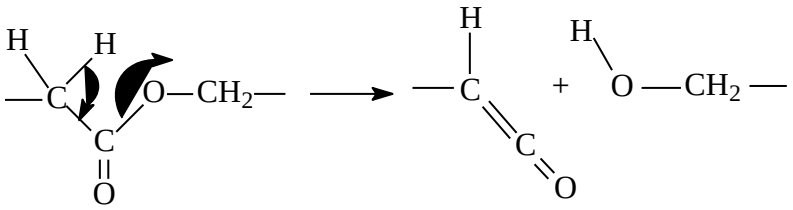
They are brittle waxes, increasing in mechanical strength at higher chain lengths. Generally, they are readily soluble in liquid ketones, amides, and phenols; moderately soluble in chlorohydrocarbons, 1, 4-dioxane, aromatic hydrocarbons, and tetrahydrofuran; poorly soluble in the lower alcohols; and insoluble in water. They

are substantially resistant to oxidation by air or ozone in normal conditions, but are degraded rapidly by ammonia, hydrazine, warm alkali solutions, and primary or secondary amines that cleave the ester linkages liberating hydroxyl groups and forming salt or amide derivatives of the carboxyl functions. The hydrophobic character of polyesters provides some physical barrier to chemical attack by water or dilute mineral acids at ordinary temperatures, but hydrolysis occurs at higher temperatures or when in contact with steam; the polymers are also prone to solvolysis by stronger organic acids such as formic acid. Some protection against hydrolysis is afforded by end-group blocking [32] or by the addition of carbodiimides [33].

The thermal stability of linear aliphatic polyesters is generally excellent up to ca 200°C. In the range of 200-250°C, particularly in vacuo and in the presence of catalysts such as halides of Mg, Sn(ll), Co(Il), Fe(III), titanium alkoxides, or antimony trioxide, these and many other types of polyesters undergo depolymerization (qv) to cyclic mono-, di-, or higher esters or lactones, a reaction that has been used as a practical synthesis for many such substances [34] . At higher temperatures (>250°C), more general decomposition ensues, typically with formation of vinyl and carboxyl groups by ester scission by a cyclic elimination mechanism (eq. 2.23); four-center cleavage to ketene groups (eq. 2.24) has also been proposed [35].



(2.23)



(2.24)

The melting temperatures of linear aliphatic polyesters increase with increased methylene:carboxylate ester group ratio in the repeating units; thus Tm for poly(ethylene adipate) is 53°C and for poly(decamethylene octadecanedioate) 92.7°C. In malonate polyesters and polyglycolide with methylene homologous repeating units, those with eve n-number values of x and y are consistently higher melting than the adjacent members with odd numbers of CH_2 groups, but the even and odd series both display the same upward trend with increasing proportion of methylene groups, eventually tending toward the Tm of polyethylene at low ester-group contents. A few polyesters have melting temperatures outside the normal range. For example, malonate polyesters, where y = 1, are very low melting, reaching Tm = 29°C only at x = 7; poly (ethylene succinate) and poly (ethylene oxalate) melt at 112 and 172°C, respectively; and polyglycolide, where x = 1, melts near 230°C. The enthalpies of fusian (ΔH_f) of the polyesters are broadly in the range of 50-90 J/g (10-20 kJ/mol of repeating unit) for materials of 40-60% crystallinity. The values increase with methylene-group content in homologous series [36]. Polymorphism is common in the series [37].

At degrees of polymerization above ~ 40, the linear polyesters are fiber forming. However, because of their combination of generally low melting temperatures, sensitivity to organic liquids, and limited hydrolytic stability, they are not used as structural materials and their mechanical properties have not been studied in detail. The materials have no specific absorptions in the visible- and normal-range UV

spectral regions, but, as esters, they show a strong and characteristic carbonyl absorbance in the IR region of 1730-1740 cm^{-1}, together with a weak overtone at double the frequency of the fundamental and a strong, rather broad absorbance due to the C-O bond centered between 1100 and 1200 cm^{-1}; accounts of the IR and Raman-active skeletal vibrations [38] and of the ^{1}H and ^{13}C NMR spectra [39] of the polyesters are available.

2.2.1.2 Substituted Acyclic Polyesters

The properties of aliphatic polyesters are markedly affected by changes in chemical structure that influence the geometrical regularity, polar character, or segmental mobility of the molecular chains.

Alkyl Group Branches; When one or more hydrogen atoms in the repeating units of malonate polyesters and polyglycolide are replaced by alkyl groups, the intermolecular separation of adjacent chain backbones is increase and there is often a reduction in the inherent symmetry of the system leading to a lowering of Tm if crystallinity is retained, and frequently to the loss of crystalline character. A typical cage is seen in the polyesterification of a linear dicarboxylic acid HOOCRCOOH with an unsymmetrical diol, such as 1, 2-propanediol $HOCH_2{}^{*}CH\ (CH_3)\ OH$, which contains two dissimilar hydroxyl groups. Since these groups show only a limited selectivity of reactivity in the normal conditions of reaction, the 1, 2-propylenedioxy groups derived from them are combined into the polyester chain with random orientations, such that the pendent methyl groups occur at either the head or the tail of successive repeating units, leading to an aperiodic spacing of the methyl groups along the chain.

Unsaturation in the Chain;When $-CH\overset{a}{=}CH\overset{b}{-}$ replaces the saturated sequence $-CH_2\overset{a'}{-}CH_2\overset{b'}{-}$ in the repeating unit, the central bond *a* is irrotatable as compared with a' (thus reducing the number of configurations available to the chain), but the adjacent bond *b* has a lower energy barrier to rotation than bond b' in the saturated system. These opposing features are further complicated by the different geometries that may be assumed by the double bond. In general, cis-vinylene groups interrupt the uniformity of structure and packing of linear chains, leading to lowered melting temperatures or to noncrystalline character. This is the cage in the maleate system which forms the basis of unsaturated polyester regina; here there is the additional feature of chemical activation of the double bond by the adjacent carbonyl group, which permits ready cross-linking. On the other hand, trans-vinylene groups cause little disturbance to the profile of polymethylene sequences 80 that crystallinity is retained. When these groups are sited within alkylene sequences of polyesters, there is little change in Tm for shorter sequences, but a reduction when these are longer; in either case, however, Tg is appreciably increased. By contrast, when the vinylene group is conjugated with the carbonyl, Tm is raised substantially as in poly (hexamethylene fumarate), which melts ~ 45°C higher than the corresponding succinate [40].

2.2.1.3 Ring-containing Polyesters

When the cyclic components, which may be aromatic, alicyclic, or heterocyclic, predominate, then the polyesters, if crystalline, have melting temperatures considerably higher than those typical of acyclic polyesters. The glass-transition temperatures are also higher, whether the materials are crystalline or amorphous.

2.2.2 Polyester Synthesis

2.2.2.1 Polyesters from Direct Esterification

Direct esterification at high temperature;

Most polyester can be obtained by direct esterification at high temperature from dicarboxylic acids and diols (equation 2.25) and from hydroxy acids (equation 2.26).

$$nHO_2CRCO_2H + nHOROH \rightleftharpoons H(ORO_2CRCO)_n + (2n-1)H_2O \quad (2.25)$$

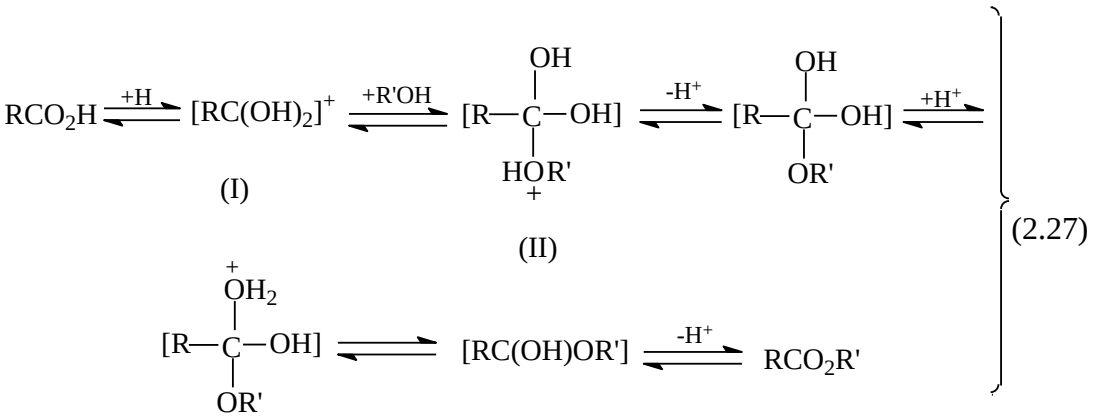
$$nHO_2CROH \rightleftharpoons H(ORCO)_nOH + (n-1)\ H_2O \quad (2.26)$$

Although reaction (2.25) usually proceeds smoothly with aliphatic diols bearing primary and secondary hydroxyl groups, it is not generally suitable for diols having aromatic and tertiary hydroxyl groups because of poor nucleophilicity and competing elimination reactions, respectively. Similarly, reaction (2.26) has been used to prepare many types of polyester from hydroxyl acids [41], but it is often unsuitable in many other cases. In fact, except glycolic and lactic acids, α-hydroxyl acids can rarely be used for direct esterification and, likewise, because of the competing dehydration reaction leading to unsaturated carboxylic acids, the attainment of polyesters by this route is prevented for most of the 3-hydroxy acids. The high temperature required for melt polymerization and the low nucleophilicity of the phenol group make this reaction generally unsuitable even for the preparation of polyesters from aromatic hydroxy acids, unless the reaction is properly activated. In general, the chemical structure of the radical to which the carboxylic group is bonded has a minor effect, and the reaction occurs easily for both aromatic and aliphatic carboxylic acids; however, bulky constituents may sterically hinder the nucleophilic addition of the hydroxyl derivative to the carboxyl group.

Both reactions (2.25) and (2.26) are 'of equilibrium', with equilibrium constants generally close to or less than unity, and, consequently, the equilibrium has to be shifted to the right by continuously removing the water throughout the course of the polymerization, in order to obtain a conversion very close to unity required to reach high molecular weights. The water elimination can be accomplished either by vacuum or by a stream of inert gas or by distilling it out of the reactor along with a part of the solvent, whose total amount is then restored in the reactor with dry solvent.

An excess of diols is often employed in order to increase the initial reaction rate; the excess diol is subsequently removed in monomeric form, via an alcohol-ester exchange reaction in the last period of polymerization, so that the initial imbalance of the functional groups does not affect the molecular weight of the final polymer.

Direct esterification can proceed at high temperature (180°C-230°C) even in the absence of added catalysts; in this case, the carboxyl groups of the monomer provide protons, which can catalyze the reaction. Small amounts (0,1-0,5 wt %) of external catalyst are nevertheless added in order to increase the reaction rate significantly; strong protonic acids (H_2SO_4), benzene-, naphthalene- and p-toluene-sulfonic acids are the most popular), oxides or salts of heavy metal ions (often acetates are preferred for their higher solubility) and organo-metallic compounds of titanium, tin, zirconium and lead are the most frequently reported catalysts. The mechanisms proposed for direct esterification of low molecular weight esters have been investigated in detail by many workers and have been discussed in detail in a review by Bender [42]. According to these investigations, reaction (2.27) is generally accepted for proton-catalyzed reactions.



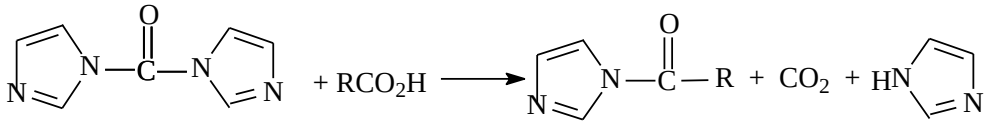
In this reaction, the reaction of the protonated form (I) of the carboxylic acid with the hydroxy compound to give the addition intermediate (II) is usually taken as the rate-controlling step. This mechanism is usually extrapolated to proton-catalyzed direct polyesterification.

Direct esterification under mild conditions;

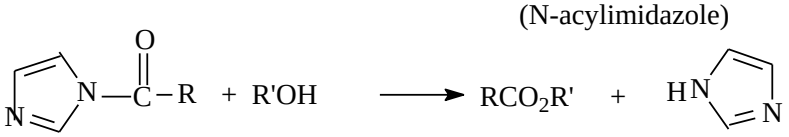
Direct esterification of low molecular weight compounds can be performed at low temperature using both strong acid and bases as catalysts; however, these conditions are not generally suitable for polyesterification. Many other catalysts have been effectively used for the preparation of esters under mild conditions, but only a few have been successfully extended to polyesters; trifluoroacetic anhydride (TFAAn), 1,1'-carbonyldiimidazole (CDI) and, more recently, phosphorus derivatives, picryl chloride and tosyl chloride (TsCl) have been used as effective promoters of direct polyesterification.

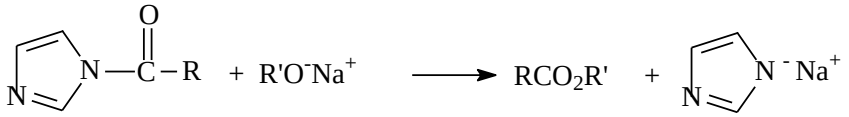
TFAAn is known as a useful rapid esterification promotor of acids with both alcohols and phenols for low molecular weight compounds.

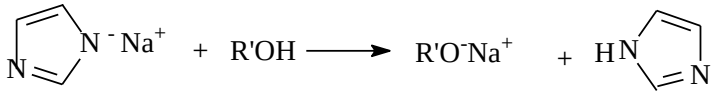
Staab prepared PET and poly (hexamethylene terephthalate) (PHMT) of low molecular weight by combining terephthalic acid and the corresponding diols with CDI in the presence of small amounts of alkoxides. The reaction occurs, in solutions of THF, DMF, chloroform and similar inert solvents. According to reactions. The N-acylimidazole, initially formed from CDI and the acid, undergoes alcoholysis according to equation (2.29). This reaction is quite slow at room temperature and the mixture must be heated at 60-70 ^{0}C, or a catalyst, such as an alkoxide, needs to be added. In the presence of sodium ethoxide, for example, the reaction is complete in a few minutes. The alkoxide, a strong nucleophilic agent, reacts rapidly with the N-acylimidazole forming the ester and imidazolylsodium; the latter, in equilibrium with alcohol, regenerates sodium alkoxide [43].


(2.28)

(N-acylimidazole)


(2.29)


(2.30)

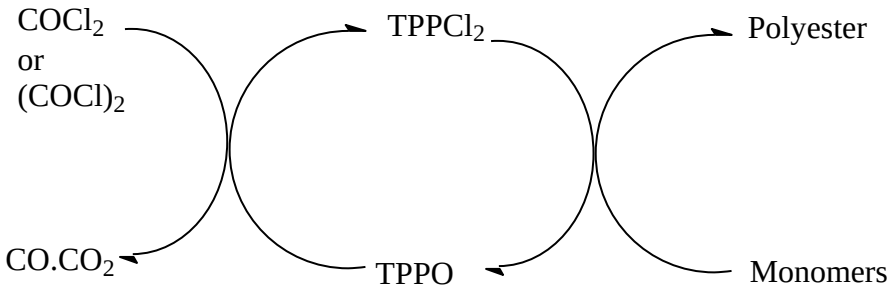

(2.31)

Substituted or unsubstituted hydroxybenzoic acids, as well as bisphenols with aromatic dicarboxylic acids, have been polymerized by these reactions in quantitative yields, at temperatures of 30- 130^{o}C, to polyesters of high molecular weight. High molecular weight polyesters containing the cinnamoyl group in the polyester backbone have also been easily prepared without affecting the thermally labile −C=C− bond of the monomer [44]. Various copoly (ester-amide) s have also been prepared successfully by these solution methods [45].

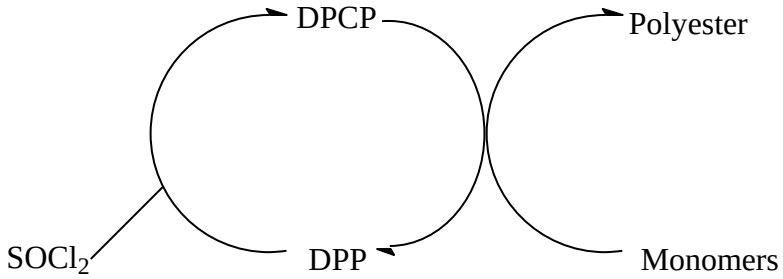
These reactions are based on the activation of the carboxyl group by condensing agents; phosphorus derivatives [46], tosyl chloride [47], and picryl chloride [48] have been successfully employed with an excess of pyridine (or other tertiary nitrogen bases), and, often, with coactivating agents. Triphenylphosphine dichloride($TPPCI_2$), diphenyl chlorophosphate (DPCP), Hexachlorocyclotri phosphatriazene (HCTPT) and phosphorus oxychloride ($POCI_3$) were found to be the most effective phosphorus compounds, and it is preferable to use these rather than the highly reactive and readily hydrolyzed acid chlorides such as PCI_5, $OSCI_2$ and O_2SCI_2.

$TPPCI_2$ and DPCP seem particularly attractive for industrial applications of the method, because they can be easily and quantitatively regenerated from their unreactive final by-products. Triphenylphosphinc oxide (TPPO) can be transformed into $TPPCI_2$ through a reaction with phosgene, or oxalyl chloride according to

reaction (2.32), Diphenyl phosphate (DPP) regenerates DPCP by reacting with thionyl chloride according to reaction (2.33) [48].



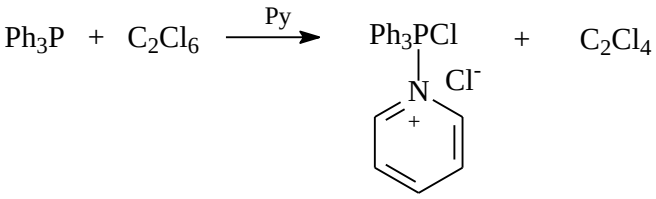
(2.32)



(2.33)

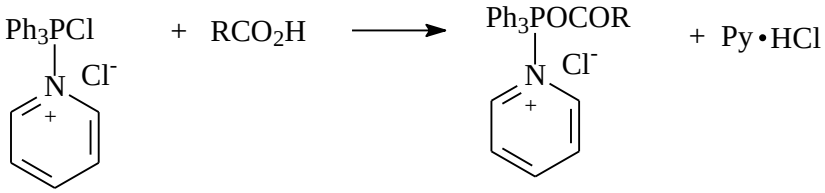
lt is well known that $TPPCl_2$ exists as an ion pair and that its phosphorus atom is attacked by nucleophilic reagents to form phosphonium salts; accordingly, it is generally assumed that in the presence of pyridine (or other tertiary nitrogen bases) $TPPCI_2$ leads to N-phosphonium salts of pyridine according to equation (2.34). Salt then reacts with carboxyl groups to give an acyloxy N-phosphonium salt according to equation (2.35). The salt produces the corresponding esters or anhydrides when attacked by hydroxy or carboxy compounds, respectively, in the presence of an acid acceptor according to equation.

The reaction of the acyloxy N-phosphonium salt with carboxyl groups with the formation of anhydride, according to equation (2.37), limits the maximum molecular weight attainable by changing the stoichiometric molar ratio between hydroxyl and carboxyl groups. It is probably for this reason that agıng tımes of more than 15 min, after $TPPCl_2$ and the acid are reacted and before the addition of bisphenol, lead to a decrease in the molecular weight of the final polyesters [49].



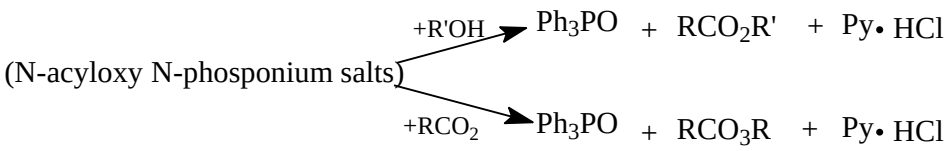
(2.34)

(N-phosponium salts of pyridini)



(2.35)

(N-acyloxy N-phosponium salts)

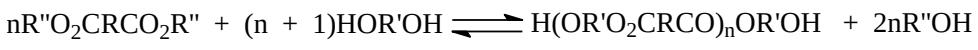


(2.36)

(2.37)

2.2.2.2 Polyesters from Alcoholysis

Most of the polyesters that can be made by direct esterification can also be prepared, and often advantageously, through an exchange reaction between ester and hydroxyl groups, usually called alcoholysis. This is a reaction of great commercial importance as most of the industrial processes of polyester manufacture proceed exclusively or in large part via such a reaction, which is schematically shown in equations (2.38) and (2.39) for AA/BB- and AB-type monomers, respectively.



(2.38)

(2.39)

Ester derivatives have lower melting points, higher solubility in diols and can usually be obtained at a higher purity grade than the corresponding acids and therefore often allow the production of better quality products and easier process control. However, higher costs, resulting from more expensive raw materials, higher energy

consumption and more expensive plants, sometimes make direct esterification more convenient, as in the case of PET [50].

2.2.2.3 Exchange Reactions between Ester and Carboxyl Groups

The exchange reaction between carboxyl and ester groups, commonly called acidolysis, is schematically represented in equation (2.40) for AA/BB-type monomers and, of course, is also valid for AB-type monomers, where R, R' and R'' can be aliphatic or aromatic. The limited number of applications of this reaction for the synthesis of polyesters is reflected in the relatively scarce literature, far less abundant than for direct esterification or alcoholysis [51].

$$nR''CO_2RO_2CR'' + nHO_2CR'CO_2H \rightleftharpoons R''CO_2(RO_2CR'CO_2)_nH + (n-1)R''CO_2H \qquad (2.40)$$

2.2.2.4 Ester Ester Exchange Reactions

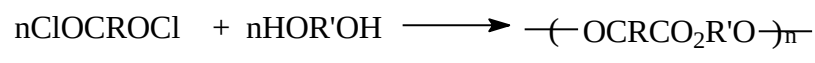
Another type of ester-exchange reaction can occur between two ester groups according to equation (2.41), This reaction, also called ester interchange double ester exchange or esterolysis, is perhaps even less studied than acidolysis and has not found any practical application in the preparation of polyesters. The main reason is probably because no eadventage are expected with respect to the reactions discussed before, as against more expensive starting materials. Nevertheless, ester-ester exchange reactions may play an important part in determining the chemical structure of copolyesters prepared or processed at high temperature and in influencing the products obtained from melt blending of different polyesters. Redistribution of chain lengths and randomization of chemical units are the consequence of intra- and inter-molecular ester-ester exchange reactions. The control of these reactions may provide a new method for the preparation of copolymers with a wide variation in microstructure directly within processing equipment [52].

$$RCO_2R'' + R'CO_2R''' \rightleftharpoons R'CO_2R'' + RCO_2R''' \qquad (2.41)$$

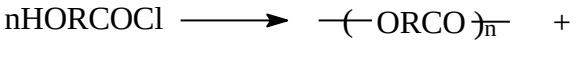
2.2.2.5 Polyesters from Acyl Chlorides

Reactions of monomers bearing acyl chloride groups with compounds having alcoholic or phenolic groups provide a useful method for polyester synthesis

according to equations (2.42) and (2.43). These reactions can be performed either at high or low temperature, though the low temperature method is by far the most widely used [53].



(2.42)



(2.43)

Temperatures ranging from 100 to > 300^{o}C can be used, depending on the reactivities of the components and the physical properties of the polymer. Under these conditions the reaction also proceeds rapidly without catalysts, and can be carried out either in bulk, (when the reactants and the polymer are law melting and miscible), or in solution, (employing a high boiling solvent and a flow of an inert gas to remove hydrogen chloride) or even in the solid state (for high melting polymers). In these cases, the progress of the reaction can be followed by titrating the hydrogen chloride removed.

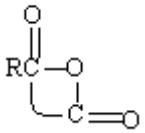
At high temperature, however, side reactions can seriously limit the attainment of high molecular weights and lower the quality of the final product. Solvent, carrier gas and reactants must be carefully dried in order to avoid traces of moisture that can lead to hydrolysis of chloroformyl groups with the formation of less reactive carboxyl groups.

For all these reasons, the reaction is preferably carried out at low temperature by interfacial polycondensation or in solution.

2.2.2.6 Polyesters from Anhydrides

Cyclic anhydrides can be useful acylating agents for the synthesis of polyesters; diols and diepoxides, or similar compounds of higher functionality, are mostly used as comonomers.The reaction with diols is shown below proceeds in two steps because the free acid, formed in the first step, is much less reactive than the original anhydride. When the reaction is carried out without a catalyst, it usually lasts many hours even at the high temperature (180-240 ^{O}C) at which it is usually performed [54]; catalysts used for direct esterification are also generally suitable for this reaction. The method is of little importance for the preparation of linear polyesters

and it is application is practically limited to the use of phthalic or maleic anhydride in the synthesis of random copolyesters and of alkyd and glycerophthalic resins. The latter are commonly prepared from phthalic anhydride and monofunctional fatty acids reacted with mixtures of aliphatic di- and poly-ols. Maleic anhydride is reacted with aliphatic diols to form unsaturated polyesters, which are subsequently transformed into crosslinked polymers through a free-radical polymerization with styrene.



$$+ \quad HOR'OH \longrightarrow HO_2CRCO_2R'OH \tag{2.44}$$

$$nHO_2CRCO_2R'OH \rightleftharpoons -(O_2CRCO_2R')_n- + nH_2O \tag{2.45}$$

High molecular weight linear polyesters have been obtained from the reaction of 1,6-hexanediol and succinic anhydride [55]. Polyesters containing free carboxyl groups have been obtained by reacting pyromellitic anhydride (1H,3H-benzo(1,2-c:4,5-c')difuran-1,3,5,7-tetrone) and ethylene glycol first in acetone and, after evaporation of the solvent, for 4 h at 100^{o}C under reduced pressure. The resulting polyester was soluble in aqueous sodium hydroxide.

2.2.2.7 Polyesters from Cyclic Ester

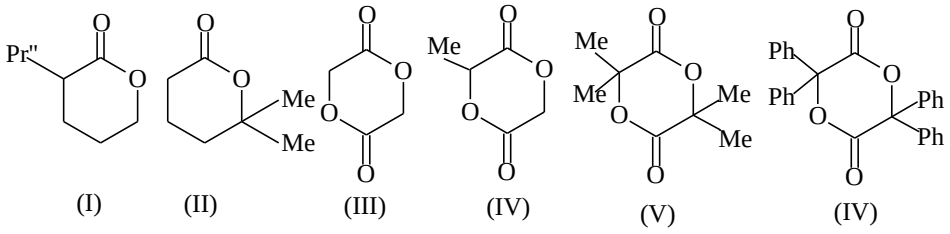
Since the pioneering work of Carothers, lactones, cyclic diesters and their alkyl- and aryl- substituted derivatives have been known to be suitable starting materials for the preparation of linear aIiphatic polyesters.

Some problems associated with the polymerization of linear monomers at high temperature, such as by-product removal, exact stoichiometry and side reactions, may be avoided in the polymerization of cyclic esters.

Their polymerization can be initiated by various types of substances and according to the initiator employed; it may proceed via cationic, anionic, coordination-insertion and 'alcoholysis' mechanisms. Ring-opening polymerization; therefore, will be limited to polymerizations proceeding by an alcoholysis mechanism which resembles

a chain rather than a step mechanism and which usually leads to low molecular weight, low melting polyesters and is therefore far less studied [56].

Polymerization of lactones and cyclic esters generally depends, to a considerable degree, on their chemical structure; that is, in particular, on their ring size and on the type and position of the substituents. High ring-strain, deriving from both angle distortion (three- and four-membered rings) or hydrogen-atom crowding within the ring (rings with more than seven or eight atoms), favors polymerization, while substituents diminish the polymerizability of these monomers by increasing the ring stability with respect to the open chain. Consequently, most of the four-, seven- and eight- membered ring cyclic esters and carbonates are polymerizable, although some substituted ones can resist polymerization. Accordingly, γ-butyrolactone, a cyclic ester with a five-membered ring does not polymerize under the usual reaction conditions, even though it has been reported that it polymerizes in 20% yield to low molecular weight polyester at 160^{o}C under a pressure of 2000 MPa. Lactones with a greater number of atoms in the ring can polymerize readily (δ-valerolactone and ε-caprolactone), or with more difficulty (3-n-propyl- δ -valerolactone (I) and 6, 6-dimethyl- δ -valerolactone) or do not polymerize at all (pentadecanolide). A similar behavior was found for cyclic diesters (polymerizability of diglycolide (III)> dilactide (IV)>> tetraphenyldiglycolide (V) and tetramethyldiglycolide (VI) [57].

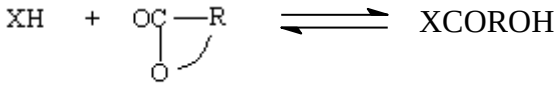


(2.46)

The size of the ring also has a very important influence on the extent to which the cyclic monomers can be converted into polyesters. For example, a substantial amount of δ -valerolactone was reported to exist in equilibrium with the polymer at temperatures exceeding 150 °C.

Equilibria occurring in polymerization proceeding via alcoholysis are shown in equation (2.47), (2.48). Active hydrogen donors, such as water, alcohols, amines and similar substances, can be conveniently used to start the hydrolytic polymerization; a

proper choice of initiator may provide a useful method of controlling the nature of the end groups. Alcohols, amines and similar monofunctional initiators lead to macromolecules with a functional hydroxyl group at one end only of the chain; water, aliphatic diols and other similar difunctional initiators give macromolecules with two functional groups and the chains grow at both ends. Initiators with more than two active functional groups may be usefully employed for the preparation of branched polyesters. In principle, the molecular weight of the resulting polyesters may be controlled by the ratio of lactone concentration to that of initiator.



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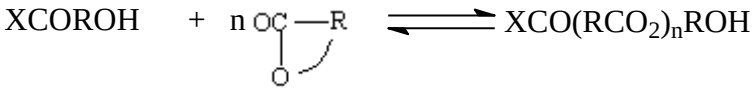


(2.48)

It has been reported that uncatalyzed polymerizations initiated with hydrogen donors occur at a relatively slow rate and give only low molecular weight polyesters; for example, the polymerization of ε-caprolactone at 190 ^{o}C initiated with ethylene glycol requires 35 h for quantitative conversion of the monomer and produces a molecular weight of only approximately 5000.

The polymerization is probably started by nucleophilic attack of the initiator on the carbonyl group of the monomer and proceeds by subsequent nucleophilic attacks of the resulting hydroxyl end-groups.

2.2.2.8 Polyesters from Biosynthesis

It is now well established that poly (β-hydroxybutyrate) (PHB) (2.49) can be synthesized by many bacteria. It exists, as a carbon reserve, in cytoplastic fluid in the form of crystalline granules about 0,5μm in diameter from which PHB can be isolated, as native granures or by solvent extraction, in an optically active form usually having a molecular weight of 10^6 or more and properties, which resembles those of isotactic polypropylene. In addition, it is noteworthy that PHB is completely

biodegradable to innocuous compounds (D (-) 3-hydroxybutyric acid) and that it is a potential source of crotonic acid by pyrolysis [58].

(2.49)

2.2.3 Characterization

Because of the multiplicity of types and grades of polyester products, there are no uniformly applicable specifications or testing standards. Individual materials are mostly appraised on the basis of criteria related to the end uses. The aspects of characterization mentioned here are therefore limited to those concerned with chemical structure and composition and molecular size.

2.2.3.1 Chemical Composition and Structure

The chemical structure of polyesters is usually apparent from the method of synthesis, but where this is unknown or where there is need to investigate the compositions of copolyesters or the possibility of side reactions occurring during polymerization, independent evidence may be required. This sometimes can be gained directly by IR or NMR spectroscopy, but more often by alkaline hydrolysis or methanolysis of the polyester to simple compounds (diols, dicarboxylic acids, hydroxycarboxylic acids, or methyl esters) identified and determined by conventional methods.

High resolution NMR methods have greatly widened the range of analytical problems that can be addressed, as illustrated by the following examples in which the ^{1}H and/or ^{13}C resonances were employed: determination of extents of inter-randomization of polyesters in the melt [59]; monomer reactivity ratios and copolymer composition in the copolymerization of glycolide with lactide; blockiness in arylate copolymers; composition determination in polyetherester blockcopolymerization; isomerization of, and glycol addition to, double bonds in the polyesterification of maleic anhydride [60].

The aberrant structural components of commercial PET, although minor in amount, are technically significant and needful of determination. Diethylene glycol unit

contents have been determined by an indirect chemical method [61], which serves as the calibration basis for the simple method of measuring melting temperature by depression. Direct determination is possible by hydrolysis or alcoholysis, followed by gc analysis or the liberated diol or silylated derivative, and at concentrations as low as 0.1 mol % by direct 400 MHz ^{1}H NMR spectroscopy of whole polymer . Methoxycarbonyl end groups remaining from incomplete ester exchange likewise are determinable by hydrolysis or hydrazinolysis followed by gc; vinyl ester end groups resulting from thermal degradation can be determined by coulometric bromination . Acetaldehyde, present in PET as a result of thermal degradation, can be measured by programmed heating of the polymer in conjunction with gc. Lastly, sensitive procedures have been described for the analysis of linear and cyclic oligomer contents in PET by lc.

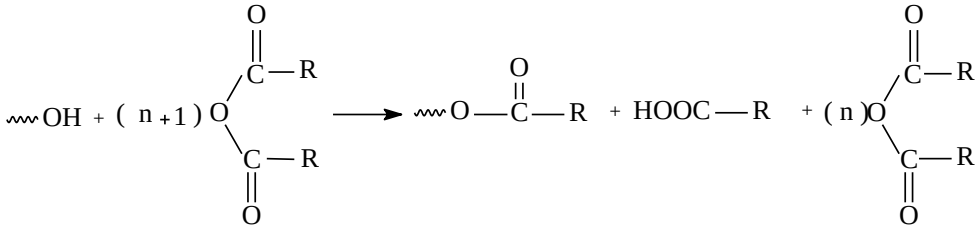
2.2.3.2 End Groups and Molecular Weights.

The molecular weights of linear polyesters are conventionally assessed by end-group analysis or by viscometry, the latter requiring independent calibration by end-group analysis or by physical methods. Traditional methods, now replaced by GPC (also requiring independent calibration) for certain polyesters [62].

Most frequently COOH and OH end groups require analysis. The carboxyl group is generally determined by alkalimetry performed in solution. Chloroform, chloroform-methanol, or 1,4-dioxane-methanol are satisfactory media for the more soluble polyesters titrated with an alkali metal hydroxide or alkoxide in an alcohol; less soluble polyesters such as PET are best dissolved in hot benzyl alcohol and then treated with chloroform to give solutions sufficiently stable at ambient temperature to be titrated with sodium hydroxide in benzyl alcohol. Other types of analyses include conversion of the COOH groups to $CONHC_6H_5$ by reaction with phenyl isocyanate, followed by determination of the aniline released on hydrolysis [63], and colorimetric determination of the uptake of basic dyes by the acid end groups

Many methods have been developed for the determination of OH end groups and may be grouped into three classes: (1) analytical chemical reactions of the hydroxyl group; (2) labeling reactions of the hydroxyl group, followed by de termination of the newly attached group; (3) spectroscopic methods. The choice of method is

influenced by the molecular weight of the polyester and by its physical characteristics, particularly the solubility. For polyesters of molecular weights up to a few thousand, which are readily soluble, hydroxyl-group contents are measured by methods based on the Verley-Bölsing procedure, involving esterification with an anhydride of acetic, phthalic, or pyromellitic acid, usually in pyridine [64]. The reagent is used in excess and the residual anhydride is hydrolyzed to its corresponding carboxylic acid, which, together with carboxylic acid released by esterification, is titrated with alkali. Equation (2.50) illustrates the relevant stoichiometry, where n = excess mol of acylating reagent.



(2.50)

The quantity sought in the analysis is thus the difference between the total COOH-group equivalent of the anhydride used, which is obtained by hydrolysis of a blank in the absence of the hydroxylic substance, and that observed when part of the reagent has been consumed by acylation. Correction must be made for the contribution of any carboxyl groups originally present in the polyester. The result is often expressed in terms of a hydroxyl number, i.e., the number of mg of KOH equivalent to the hydroxyl groups present in each g of the polyester; another conventional expression is g OH group/10^6 g polymer. Related methods include treatment with an excess oftrifluoroacetic acid followed by Karl Fischer titration of the liberated water of reaction and enthalpimetry of the acylation reaction.

Polyesters such as PET, which are inadequately soluble in the above reactant systems, can be acylated with 3,5-dinitrobenzoyl chloride in hot nitrobenzene, followed by hydrolysis of the excess reagent and titration of the liberated dinitrobenzoic acid . Alternatively, reaction with succinic anhydride in hot 1-methylnaphthalene converts each hydroxyl group to its succinate hemiester

-----OOC $(CH_2)_2$COOH, which can be recovered and titrated with alkali to give the equivalent weight of the OH groups originally present.

Labeling-derivatization methods for hydroxyl-group contents include conversion with phenyl isocyanate to phenylcarbamoyl groups determined by NMR spectroscopy;

IR spectroscopy made an early contribution to the determination of COOH and OH end groups in PET [65]. The absorbances of these groups at 3256 and 3542 cm^{-1}, respectively, can be used to measure concentrations in polyester film with an accuracy claimed to be twice that obtained by titration methods. ^{1}H NMR spectroscopy has likewise been adapted for hydroxyl end-group analysis, e.g., with the use of a europium-shift reagent, and notably by converting the OH groups to their trimethylsilyl derivatives, which contain nine methyl-group protons for each initial hydroxyl-group proton, thus greatly amplifying the signal available for measurement.

The total concentration (X) of end groups in a linear polyester (expressed in g equivalents/$l0^{6}$ g polymer) is related to the number-average molecular weight by $M_n = 2 \times 10^{6} / (X)$, and average molecular weights are correlated with the limiting viscosity number of the polymer in solution by $[\eta] = KM_n$.

2.3 Unsaturated Polyesters

Unsaturated polyester resins are step-growth polymers formed by the interaction of stoichiometric mixtures of unsaturated and saturated dibasic acids or anhydrides with dihydric alcohols or oxides. The unsaturated acid component is fundamental to the reactivity of the low molecular weight polymers formed and is derived primarily from 1, 2-olefinic dibasic acids such as maleic acid or anhydride.

The commercial resins have established a significant position within the plastics industry. They are typically solutions of unsaturated polyester polymers dissolved in unsaturated coreactant liquid monomers such as styrene to enhance reactivity and processibility. Free-radical catalysts initiate cross-linking reactions involving the unsaturated polyester polymer and the unsaturated co-reactant monomer, rapidly transforming the low viscosity resin into a rigid thermoset plastic state, and comprising a three-dimensional polymer network.

The degree of unsaturation in both the polyester polymer and liquid monomer determines the complexity and physical characteristics of the cross-linked network, although properties such as hardness, flexibility, heat resistance, fire retardance, and others can be modified by substitution with glycols and saturated dibasic acids into the polyester polymer backbone [66].

Although other unsaturated monomers can be more effective in enhancing specific properties of the cross-linked plastic, styrene, in accordance with general cost-performance criteria, is the principal co-reactant monomer in commercial formulations.

The evolution in petrochemistry since 1945 has provided an extensive range of raw materials for polyester resin synthesis, resulting in the development of a family of resins whose composition and performance versatility are unmatched by most other polymeric materials.

The success of unsaturated polyester resins in fabricated composites has been achieved in conjunction with glass fiber or other types of reinforcing material. The terms fiber glass-reinforced plastic (FRP) or glass fiber-reinforced plastic (GRP) are used interchangeably for cross-linked polyester plastic materials.

In the late 1980s, the consumption of unsaturated polyester resins in North America

Exceeded 500 x 10^3 metric tons annually; consumption in Asia is similar. Polyester products are used in many markets of commercial significance, ranging from automotive to construction and electrical applications. Structural applications consume ca 80% of production; the remainder is used without fibrous reinforcements, but usually extended with inexpensive fillers primarily for producing cast items.

In early research, polyester resins formed by condensing tartaric acid, glycerol, succinnic acid, and salicyclic acid supplied the basis for many scientific studies. Reactions between glycerol and phthalic anhydride were also investigated, and when these compositions were modified with the fatty acids of unsaturated vegetable drying oils for use as protective coatings, their commercial potential was recognized.

Carothers in his classical studies succeeded in defining the stoichiometric relationship inherent in step-growth condensation polymerization and developed the basic technique for the manufacture of these early polyester resins. Attempts to improve the drying characteristics of these unsaturated products expanded the knowledge of oxidative hardening. The concepts of polymeric cross-linkage were introduced to account for the behavior of certain polyester derivatives of maleic, fumaric, and citraconic acid, which hardened to an infusible state when heated.

Parallel developments in synthetic rubber chemistry and the emergence of addition polymer technology led to the discovery of the influence of vinyl monomers on cross-linking involving polyesters derived from maleic anhydride [67].

Styrene solutions containing unsaturated polyester polymers derived from maleic anhydride were commercialized in 1942, when the U .S. Rubber Co. used these resins in combination with glass fiber reinforcements to manufacture protective coverings for radar receivers. The emergence and growth of the petrochemical industry following the end of World War II inspired research on unsaturated polyester resins, and by 1955 the basic technology had been established, remaining essentially unchanged to the present.

2.3.1 Raw Materials

Petrochemicals supply most functional derivatives used for the manufacture of polyester resins. Lower glycols are derived almost exclusively by the oxidation of ethylene or propylene. Aromatic dibasic acids are produced by the oxidation of xylenes and maleic anhydride by the oxidation of benzene. Styrene monomer is manufactured on a large scale from benzene and ethylene. Initially, unsaturated polyesters were simple compositions of propylene glycol, phthalic anhydride, and maleic anhydride. Dissolution of this viscous precursor in styrene monomer produced resins of low viscosity that was adaptable to simple fabricating processes under ambient conditions. This classical formulation has remained essentially unchanged and is typical of most industrial processes. This family of unsaturated polyester resins is known as (ortho)phthalic resins or general-purpose resins in view of their chemical derivation and wide adaptability and performance characteristics. Even though commercially successful in a wide variety of applications, the phthalic

resins exhibit certain limitations with regard to heat resistance, fire retardancy, resistance to chemical attack, and processibility.

By a process of substitution, new families of polyester resins have evolved with improved and specialized properties, characteristic of certain organic constituents. Aromatic derivatives such as isophthalic and terephthalic acid or diols derived from bisphenol A provide a higher degree of hardness, rigidity, and enhanced thermal characteristics. Aliphatic constituents such as adipic acid, 1, 4-butanediol, and diethylene glycol yield soft, pliable products. Property modification is influenced by the number of methylene or oxyethylene units separating the reactive functionality. Other charecteristics are derived from reactive halogenated compounds which impart flame resistance.

Highly branched aliphatic or substituted aromatic derivatives introduce steric effects around the double bond, which reduces its ability to cross-link with styrene or other monomers; 2,2,4-trimethyl-l,3-pentanediol is particularly not able in this respect. α-Methylstyrene is similarly influenced by the pendent methyl grouping on the double-bond carbon, which impedes its reaction rate during the cross-linking with fumarate groups.

Early unsaturated polyester resin compositions were typical in the choice of styrene as the unsaturated monomeric solvent for the highly viscous or solid unsaturated polyester polymers. Styrene monomer compared with other commercial monomers usually offers equivalent properties at much lower cost. Certain monomers enhance specific properties, e.g., triallyl cyanurate and diallyl phthalate [68] extend the thermal durability required in certain electric components. These unsaturated polyester-monomer compositions are known as allyl resins. Other monomers, such as vinyl toluene, methyl methacrylate, p-t-butylstyrene, o-chlorostyrene, and a-methyl styrene, find only limited utility, usually in combination with styrene.

In most commercial formulations, the reactivity of the polyester polymer is derived primarily from the maleic anhydride component. Maleic anhydride is the most economic derivative, although fumaric acid can be substituted, yielding resins with the same properties but some subtle structural differences. Other unsaturated acids such as itaconic acid, methacrylic acid, and acrylic acid are also used.

Tetrahydrophthalic acid or anhydride and cyclopentadiene-maleic anhydride adducts, although unsaturated, do not enter into copolymerization reaction with styrene and cannot be substituted for maleic anhydride. The unsaturation in tetrahydrophthalic anhydride contributes to the air-drying characteristics of the resin. Bisphenol ether derivatives are exceptional in their resistance to corrosive chemicals and high temperatures, and usually appear in formulations without a saturated dibasic acid component.

Exposure to heat or light may result in uncontrolled cross-linking and an increase in viscosity. Ultimately, a semi plastic solid or gel forms that cannot be utilized. The polymerization reactions occurring are free radical initiated. The active radicals are formed by exposure to oxygen. Oxygen addition across the styrene double bond produces hydroperoxides, which initiate the polymerization reaction. These hydroperoxides are transformed into peroxides and, in resins dissolved in styrene monomers, eventually into benzaldehyde. Therefore, poly- ester resins exposed to air exhibit a characteristic benzaldehyde odor. Oxygen- initiated free-radical formation can be suppressed by free-radical inhibitors such as quinones or other substituted phenols. Benzoquinone at concentrations as law as 150 ppm suppress any tendency for premature gelation at ambient temperatures and extend the shelf life to at least 6 months. However, because of the toxicity of benzoquinone, other inhibitors such as hydroquinone or toluhydroquinone are employed in the manufacturing process, where the blending of the polyester resin with the reactive monomer needs to be stabilized to prevent gelation at the high process temperatures.

2.3.2 Manufacturing Process:

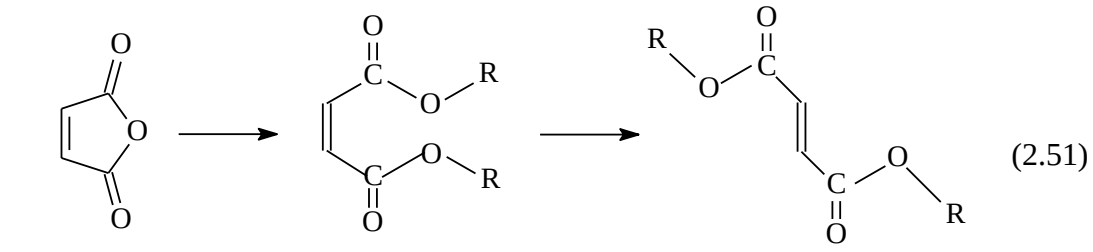
2.3.2.1 Fusion-Melt Process

Fusion melt is the conventional process for condensing liquid glycols with dibasic acids of low melting temperature, including phthalic anhydride, aliphatic dibasic acids, and various halogenated intermediates. The reaction is carried out with stoichiometrically balanced formulations; the glycols and dibasic acid can be substituted by other components of similar functionality.

Propylene glycol, phthalic anhydride and maleic anhydride are added in liquid form to facilitate loading. The molten anhydrides enter the reactor after the glycol, saving the heating time needed when solid anhydrides are used. Heat is supplied by hot oil circulating through internal coils. Agitation is maintained throughout the reaction to dissipate heat and promote the evolution of water vapor into the condenser system. The rates of polyesterification are influenced by the structures and stoichiometry of the glycol and dibasic acid components, which react according to third-order rate kinetics. Although the initial formation of law molecular weight oligomers is rapid, the progressive development of higher molecular weight polymers approaches an asymptotic limit, resulting in extended reaction periods. For fusion-type reactor processes, phthalic resins require 15 h at 190°C to attain a satisf'actory molecular weight. The reactor must be designed to free the viscous melt of water, which retards the reaction.

Maleic anhydride has reactive double bonds, the maleate ester derivatives do not homopolymerize during processing. However, the reaction of maleic anhydride with glycols [69] produces derivatives of higher functionality that may promote gelation at 190°C.

Formulations with high concentrations of maleic anhydride ultimately lead to a net reduction of ca 15% in the ungaturation of the resulting polymer. Fumaric acid does not give side reactions and retains a higher degree of unsaturation when substituted into comparable formulations. The polymer products have higher reactivities and superior properties. Maleic anhydride or fumaric acid confers the fundamental unsaturation to the polyester, which provides the reactivity with coreactant monomers such as styrene. Maleic anhydride exists in a planar configuration of low conformational energy, and the conversion into maleate diesters and oligomers during the initial esterification reaction increases the strain energy across the double bond because of steric hindrance. At lower reaction temperatures, ie, 160°C, the maleate esters remain in this condition, but as the reaction temperature exceeds 180°C they effectively relieve the strain by transforming to the more planar trans-fumarate isomer, which reduces the streric congestion



(2.51)

maleic anhydride cis-maleate ester trans-fumarate

In conventional fusion melt, the long reaction time, usually at temperatures above l80°C, causes the maleate ester to isomerize to the corresponding fumarate, especially in the presence of branched secondary glycols such as propylene glycol [70]. Bulky aromatic dibasic acids also promote the isomerization mechanism by subjecting the maleate double bond to increased strain caused by localized steric effects.

In contrast, when the linear ethylene and diethylene glycols with primary hydroxyl groups are utilized in reactions with maleic anhydride, the condensation reaction proceeds more rapidly at lower temperatures, producing the desired polymer in much less time. The isomerization of maleate to fumarate may only be partially complete, which is reflected in the product. Maleate esters, because of the increased strain across the double bond, are distorted slightly from a planar configuration, which suppresses their ability to copgIymerize with styrene monomer. The corresponding fumarate polymers are subject to less steric interference in the transform and are able to assume a planar configuration, displaying reactivities almost 20 times those of the maleate reaction products in subsequent copolymerization reactions with styrene [71].

The isomerization of maleate esters and oligomers to the corresponding fumarate derivatives during the polyesterification process is of fundamental importance in the development of optimum physical characteristics.

2.3.2.2 Oxide Process

The esterification between glycols and dibasic acids is a reversible reaction whose rate and equilibrium point are determined by the removal of condensate water. Esterification becomes more difficult with increasing viscosity, suppressing the

mobility of the reactants and the escape of water. Recent processes use glycol oxides (monoepoxides) and acid anhydrides, which react rapidly to form linear polyester resins without the formation of by-product water.

Mixtures of propylene oxide, maleic anhydride, and phthalic anhydride can remain in liquid form at 100°C without a reaction-taking place. Esterification catalysts initiate a highly exothermic step-growth polymerization in which the final molecular weight is controlled by the initiator concentration. In view of the volatility of propylene oxide, the reaction is usually conducted at 6.89 MPa

(100 psi) and ca 160°C. Because of its higher vapor pressure, ethylene oxide is not used in these formulations; other oxide derivatives such as epichlorohydrin are too expensive.

Lithium carbonate and zinc chloride catalysts produce polyester derivatives with distinctive compositional variations. Lithium and related basic salts promote the step-growth sequence alternating between oxide and anhydride, where as acidic zinc chloride promotes polyetherification of the monoepoxides as well as the expected polyesterification. Polymers derived in the presence of zinc chloride require high stoichiometric ratios of the monoepoxide to balance the acid component. The resulting product has properties characteristic of ether glycol derivatives.

The highly exothermic reaction between the functional end groups of the growing polymers and the monomeric reactants occurs rapidly. To exercise control over the reaction, the propylene oxide is usually added to the other reactants over a certain period; no external heating is required.

The self-contained nature of the process and the absence of condensate contaminated with chemical effluents are advantageous from a pollution standpoint. The process provides for the 100% conversion of the reactant into finished products, whereas the phthalic fusion-melt process gives yields below 95% because of by-product losses.

The low reaction temperatures, i.e., 160°C, result in low transesterification rates, and phthalic esters are capable of achieving higher molecular weights than by comparable fusion processes. Isomerization of maleate to fumarate does not proceed

to any significant degree, and even though of sufficient molecular weight, solutions of these maleate polyesters in styrene are not sufficiently reactive to find commercial utility as cross-linking polymers. These high molecular weight maleate polymers do not isomerize as easily as the lower molecular weight maleate esters formed by the fusion melt. The isomerization of maleate to fumarate is only 10% completed even at 18O°C. Isomerization catalysts such as piperidine and morpholine at 1-2% concentration give >7 % fumarate, but heating 2-3 h at 18O°C darkens the resin, which is unacceptable in many commercial appli- cations. Even in the presence of isomerization catalysts, oxide resins never attain a fumarate concentration as high as resins produced by fusion melt. Cross-linked phthalic resins produced by the oxide process have characteristically tower reaction rates. The oxide process produces fewer final products and cannot be adapted for the inclusion of isophthalic acid, adipic acid, or diethylene glycol.

Multifunctional initiators such as glycerol or pentaerythritol form branched polymers that do not form gels, as obtained by fusion. These "star polymers" do not exhibit any unusual characteristics that may be expected from their structure.

2.3.2.3 Cross-linking Mechanism

Catalysts and Initiator Systems**;**

The resin is transformed from a stabilized liquid into a rigid plastic state; free-radical catalysts, e.g., ketone hydroperoxides or benzoyl peroxide, initiate a controlled cross-linking reaction involving the fumarate polymer and styrene monomer. The catalysts are activated by heat, multivalent metal accelerators, or tertiary aromatic amine promoters, which decompose the peroxides into free radicals. However, the free radicals are initially consumed by quinone stabilizers and polymerization does not proceed until the inhibitor system is completely neutralized. Then, the liquid resin is quickly transformed into a soft rubbery gel. As cross-linking proceeds, heat is generated as the soft rubber is transformed into a hard glassy plastic containing a cross-linked, three-dimensional polymeric net- work. The most frequently used initiator system at ambient temperature includes methyl ethyl ketone hydroperoxides and styrene-soluble, multivalent metal-salt accelerators, such as cobalt naphthenate or octoate. Other systems requiring more time include cumene hydroperoxide plug

manganese naphthenate. Without accelerators, diperoxides and diperesters require higher temperatures. Benzoyl peroxide, however, can be used at room temperature in the presence of tertiary aromatic amine promoters. Such systems are employed for applications at low temperatures. Dissociation of hydroperoxide catalysts into free radicals at ambient temperature involves reduction-oxidation (redox) reactions. Redox initiator systems involving metal-salt derivatives are effective with organic hydroperoxide derivatives, e.g., MEKP, but ineffective with diperesters or diperoxides such as benzoyl peroxide at ambient temperatures.

$$\left.\begin{array}{l} Co^{3+} + ROOH \longrightarrow RO^{\cdot} + O^{0} + H^{+} + Co^{+2} \\ Co^{2+} + ROOH \longrightarrow RO^{\cdot} + OH^{-} + Co^{3+} \end{array}\right\} \quad (2.52)$$

Free radicals are produced from hydroperoxides by cobalt in either valent state; this action is enhanced by tertiary aromatic amines [72], which appear more effective in promoting the transition of cobalt from the higher to lower valency state.

Of the common multivalent metal accelerators, only cobalt, manganese, and vanadilim derivatives have the necessary potential to activate hydroperoxides at ambient temperatures, although monovalent metal salts derived from lithium and zinc behave in a synergistic capacity, modifying subtle features of the gelation mechanism. Soluble copper salts exert n pronounced effect in the presence of cobalt-hydroperoxide initiator systems, suppressing the cross-linking at concentrations as low as 100 ppm and even preventing gelation at much higher concentrations, i.e., 500 ppm. Acetyl hydroperoxides show particular sensitivity to copper.

Gelation and Cure;

Initially, the free radicals produced by the redox systems are neutralized by quinone stabilizers present in the resin system. After an induction period, the free radicals initiate cross-linking polymerization involving the fumarate groups in the polyester chains and the unsaturated styrene monomer. This so-called gelation time is defined as the period between the addition of the initiator system to the liquid resin and the appearance of a soft intractable gel, where 1-2% of the polymer has been cross-

linked. Crosslinking proceeds rapidly and establishes the structure of the three-dimensional network in which polymers and monomer are immobile. The corresponding decrease in termination rate constant and net increase in free-radical concentration leads to an exponential jump in styrene-initiated copolymer growth. The gel effect gradually transforms the mass to a rubbery transition phase. As cross-linking and copolymer formation accelerate, heat is generated and a rigid plastic forms. The activation energy of the gelation and cross-linking is estimated to be 50 kJ/mol (12 kcal/mol), and the overall reaction rate constant 2.7 x 109 exp (- 17, OOO/RT) min^{-1}.

Commercial polyester resins usually contain 35-45% styrene, corresponding to a stoichiometric relationship of approximately two styrene units for each fumarate unit. Optimum physical properties are obtained around this ratio, although reactions between styrene and fumarate esters in dilute solutions appear to favor an alternating addition sequence. Initial copolymer development in poly- ester resins also favors this mechanism, but the rapid formation of the physical gel at the onset of cross-linkage immobilizes the polymer and fixes the remaining fumarate moiety. The remaining styrene monomer bridges the space s between the fumarate unsaturation in the copolymer network. The complexity of the gel develops rapidly as increasing numbers of styrene radicals initiate polymerization, and the copolymers propagate radically in independent micellular structures. Localized fumarate groups within the micelle rapidly disappear and form copolymers with alternating units, but as the polymer expands within the micelle, combinations, including higher numbers of styrene units, prevail until polymerization is terminated at the boundaries with other expanding micellular networks. Raising the styrene content above 45% increases the distribution of styrene homopolymer blocks in the fumarate copolymer and it is suggested that most copolymerizations terminate in a styrene homopolymer block. Apparently, styrene does not enter into homopolymer formation independent of cross-linking. No polystyrene polymers have been extracted, even in polyester resins containing 60% styrene monomer. In spite of the steric constraints imposed by the physical gel, all fumarate groups are able to combine with styrene in the development of the network. Maleate polymers, on the other hand, having lower reaction rates with styrene and high steric factors because of the cis spacial arrangement, form networks containing unreacted maleate groups and a higher

distribution of styrene homopolymer blocks within the copolymer. Maleate polymers cross-linked with styrene consequently generate less exotherm and remain in a rubbery transition state for longer periods. The final plastic is less rigid and has lower modulus and softening temperatures than the fumarate polymer. Electron microscopic studies of cross-linked polymers reveal [73] highly crosslinked crystalline regions overlapping at amorphous boundaries of much lower crosslink density. The network is not a unit structure bul an overlapping system of many small networks (Fig. 2.1). The nature of the amorphous boundary areas is of fundamental importance in the determination of intrinsic properties.

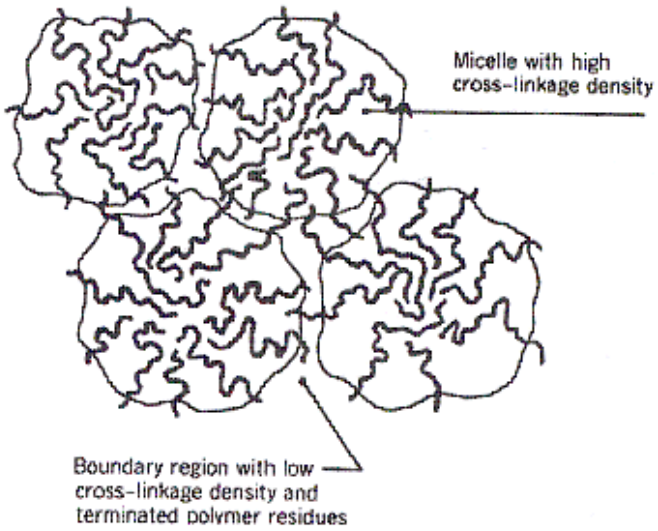


Figure (2.1) Styrene-fumarate copolymers growing radically from micellular structures terminating at common boundaries.

The rate of the gel-structure development depends on the free radicals available after neutralization of the inhibitor system. The complexity of the gel increases as the degree of cross-linking progresses, and enters a rubbery transition state of surprising friability. As the mass begins to heat up. the hardness increases rapidly and other physical characteristics develop quickly as well. The cross-linkage network is 95% complete after the he at dissipates from the mass; further heating (post-cure) at higher temperatures driver the reaction to completion. Without post-cure, the plastic exhibits a distinct styrene odor, which may persist for weeks.

3. EXPERIMENTAL

3.1. Chemicals

Maleic anhydride (E. Merck), 1-hydroxy 2, 3-epoxy propane (Glycidol) (Acros Chemicals). All these chemicals were analytical grade commercial products. They were used as supplied Styrene (E.Merck) was made inhibitor-free by shaking with 5 % NaOH solution and dried with anhydrous $Na_2 SO_4$. Dimethoxyethane (Fluka) was distilled before use. Diethyl ether was distilled before use.

3.2 Instrumentation

a) Nuclear Magnetic Resonance (^{1}H-NMR)

Spectra were recorded by a Bruker 250-MHz spectrometer using acetone-d_6 as solvent and tetramethyl silane (TMS) as internal standard.

b) Gel Permeation Chromatography (GPC) traces was taken Agilent 1100 with RI detector. Waters styrogel columns (HR 4, HR 3, and HR 2) were used at flow rate of 0.3-mL/ min. The eluent was tetrahydrofuran (THF).

c) Differential Scanning Calorimeter (DSC) thermograms were taken by Perkin Elmer DSC6 (at a heating rate of 5^0C/min, under nitrogen)

d) Infrared Spectra (FT-IR)

Spectra were obtained by Mattson 1100 FT-IR Spectrometer.

3.3 Synthesis of Monoglycidyl maleate:

The first step product of the maleic anhydride-glycidol reaction was obtained as a waxy product as follows. Thus, 3.7 g (5.10^{-2} mol) glycidol (2-3 epoxy 1-propanol), 4.9 g (5.10^{-2} mol) maleic anhydride and 4 ml of dimethoxy ethane (ethylene glycol dimethyl ether) were placed in a 50 ml volume of flask. The flask was mounted in a thermostated oil bath at $70^0 \pm 3^0$C. The mixture was stirred for 45 min. After cooling,

the reaction content was poured into n-heptane or diethylether (30 ml). The white precipitate was separated by decanting. The residue was dissolved in 4 ml of dimethoxy ethane and reprecipitated in diethyl ether. Resulting product was dried at 40^0C under vacuum for 24 h.yield of wacsy product was 7.3 g. (84.9 %).

3.4 Preparation of Soluble Polyester from Maleic anhydride and glycidol :

Polyesterification of maleic anhydride with glycidol was carried out either by stepwise heating at 80^0C and 120^0C (method A) or direct heating at 120^0C (method B).

Method A:

Maleic anhydride (24.5 g, 0.25 mol) was dissolved in the mixture of glycidol (18.5 g, 0.25 mol) and dimethoxy ethane (15 ml) in a reaction flask equipped with a reflux condenser and $CaCl_2$ guard tube. The flask was placed in thermostated oil bath preheated at a constant temperature of 80^0C. The mixture was stirred for 45 min. Then temperature of the oil bath was adjusted to 120^0C and stirring was continued for another 45 min. Viscosity of the mixture gradually increased. Then the flask was removed from the oil bath and cooled to room temperature. The resulting viscous solution was optically clear and no significant viscosity change was observed after standing in a closed bottle for a week at room temperature.

^{1}H-NMR spectrum of the polymer is given in fig.2.

Intrinsic viscosity of the polyester in dimethoxy ethane was found 0.034 dL g^{-1}. GPC indicates a molecular weight of Mn = 16400 and Mw = 17200 (fig. 3) the product is soluble in water, ethanol, acetone, DMF, THF and insoluble in benzen, toluene, ether and n-heptane.

Method B:

The same procedure was followed except the mixture was heated at 120^0C for 45 min.

Polymers obtained by heating for prolonged times are partly soluble in water.

4. RESULTS AND DISCUSSION

4.1 Determination of the carboxyl content by using Monoglycidyl Maleate:

Carboxyl content of the above product was determined by the conductometric titration with 0.1 M NaOH solution. The product (0.67 g.) was dissolved in water and diluted to 100 ml in a volumetric flask. 50 ml of this solution was titrated with 0.1 M NaOH solution. The titrant (19.1 ml) consumed corresponds to 5.7 mmol carboxyl group per gram of the product. Theoritical value expected for the monoglycidyl maleate (Mw = 172) is about 5.813 $mmolg^{-1}$. Ratio of the two (5.7 / 5.813) = 0.98, which is very close to unity. ^{1}H-NMR spectrum of the product is given in fig.2a.

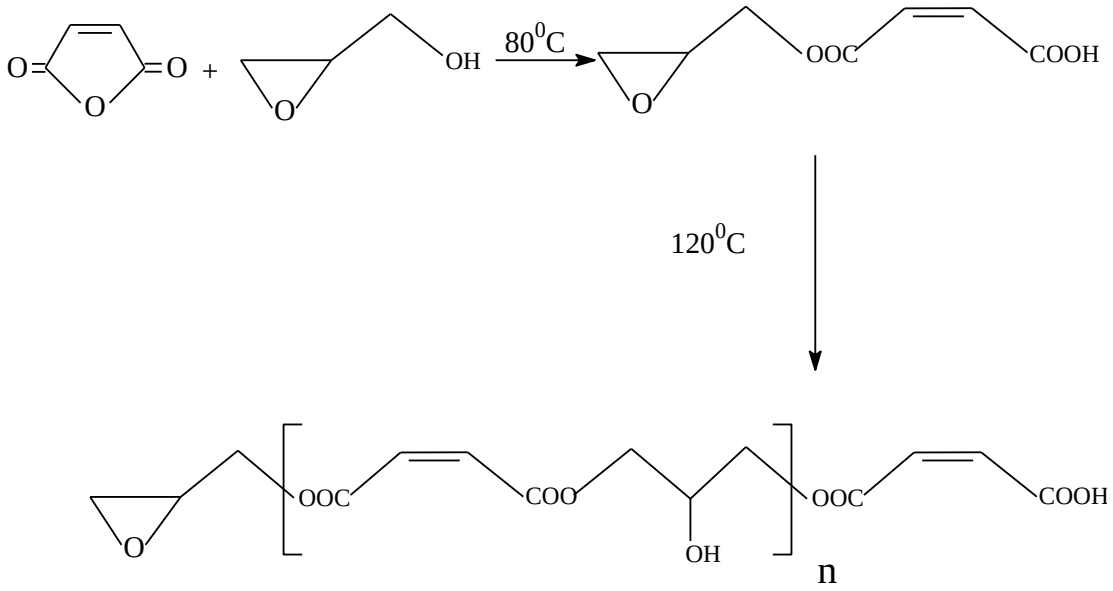
4.2 Synthesis of Soluble Polyester from Maleic anhydride and glycidol

Controlled reaction of maleic anhydride with glycidol in dimethoxyethane gives soluble polyesters (Scheme1). Since polyester formation in this reaction proceeds without water elimination, highly viscous clear solutions can be obtained in reasonably short periods, i.e. 2-3 h.

The reaction without solvent, however, results always in cross-linked insoluble products. Many attempts in preparing soluble polyester without solvent were failed. This must be due to exothermic nature of the reaction. Because, in this case heat dissipation by stirring becomes almost impossible due to increasing viscosity of the mixture and sudden rise of the temperature leads to further reactions yielding cross-linked structures. Hence, the use of solvent is essential for preparing soluble polyesters.

The polyester formation must proceeds in two steps; i) reaction of MA with hydroxyl group of GL, ii) ring opening of the epoxy group to react with free carboxyl group.

The two-step mechanism was evidenced by DSC. DSC traces of maleic anhydride-glycidol mixture (fig1) represent two exotermic peaks below 150^0C. These peaks observed at 80 ^{0}C and 120^0C must be associated with the first and second steps respectively. In order to prove this assumption we have compared DSC thermo grams of MA- n-butanol and GL-phtalic acid mixtures with those of the MA-GL mixture. However, the MA- n-butanol and GL-phtalic acid mixtures gave exotherms at 100^0C and 110^0C. Although mono-esterification temperature of MA is somewhat lower than that of ring opening of the epoxy group, this result is not satisfactory to make such an assignment.



Scheme 1: Synthesis of the self-curable polyester

Nevertheless the stepwise reaction scheme was verified by isolation of the first step product formed at 80^0C. It is fact that isolation of this reaction intermediate is very difficult, due to sudden rise of the reaction temperature. This was achieved by adjusting the bath temperature at 70^0C. Inner temperature of the equemolar MA-GL mixture in dimetoxyethane, in these conditions, reaches around 80^0C, due to contribution of the heat evolved from the exothermic reaction. Vigorous stirring for 45 min. and subsequent precipitation in ether gave a white waxy product. Attempts for crystallization of this product were failed. However conductometric titration of the product (with 0.1 M NaOH) indicated a %98 of pure monocarboxyl compound. Also ^{1}H-NMR spectrum of this intermediate (figure 2a) establishes the monoglycidol maleate structure.

These results revealed that, the polymerization proceeds by two-step reaction scheme and the first step occurs at 80^0C and gives monoglycidol maleate. As a result, linear polyester can be prepared either by heating in two steps at 80^0 C and 120^0C or by direct heating at 120^0C. Indeed, both procedures give soluble polyesters when equemolar mixtures of maleic anhydride and glycidol are reacted in aprotic solvents such as dimetoxyethane, DMF and NMP. Having low boiling temperature dimetoxyethane is better solvent.

Formation of the mono-glycidyl maleate intermediate and subsequent polyesterification can be followed by NMR spectra of the corresponding products. Thus, ^{1}H-NMR spectrum of the intermediate (figure 2a) establishes the monoglycidyl maleate structure. Non-equivalent protons of the maleate groups are observed at 6.4 and 7.4 ppm. Other aliphatic proton signals are located in 3.3 – 4.3 ppm range. Integral ratio of these group signals is 1/ 3 as expected. Whereas carboxyl protons do not give a visible peak or band as usual.

^{1}H-NMR spectrum of the soluble polyester prepared in dimetoxyethane (figure 2b) shows a single peak for equivalent protons of maleic double bonds at 7.1 ppm. This is clear-cut evidence for the polymerization of monoglycidyl maleate. New signal emerged at 2.7 ppm in fig2b is due to the methine protons of the carbinol group resulting form ring opening of the oxirane function.

The integral ratios of those peaks are also in consistent with structure of the polyester proposed. However, it is difficult to make an assignment for the maleate-fumarate isomer ratio based on location of the proton signal of the double bond. Because proton signals of the fumarate isomer does not appear around 6.8 ppm. Regarding with low field shift of the double bond protons, one can assume that the signal at 7.1 ppm originates mostly from maleate structure. Most probably such an isomerization is being prevented by the controlled process.

These results clearly indicate that soluble polyesters can be prepared by controlled reaction in dimetoxyethane.

GPC trace of the polyester (Figure 3) obtained by heating at 120^0C in dimetoxyethane for 1 hour indicates a molecular weight of Mn=.6200 with a polydispersity index of 1.012. Intrinsic viscosity of this product is $[\eta] = 0.12$ dLg^{-1}.

Corelarion of the intrinsic viscosities with the molecular-weight data (from the GPC), Mark-Houwing parameters of the polyester were estimated to be;

$K = (7.4 \pm 0.1).10^{-4}$ and $\alpha = 0.42 \pm 0.02$ (at 30^0C, for dimetoxyethane solvent)

Many polymers with different viscosities can be prepared depending on the reaction periods. But two hours of reaction period is enough to obtain polyesters with appreciable viscosities. Of course one can obtain different molecular weights of polyesters using various solvent ratios in different reaction times (table1). The molecular weights attained are proportional to the reaction times.

Table-1: Characteristics of the soluble polyester formation.

Sample	**Monomer Ratio a (%(w/w))**	**Reaction time at 70^0C b**	**at 120^0C b**	**Limit c viscosity [η]**	**Mn d**	**Mn/Mw**
1	86	—	120	0.037	11700	1.06
2	90	—	60	0.049	22700	1.04
3	90	90	30	0.034	16400	1.05
4	90	90	60	0.045	17500	1.01

(a): Percentage total mass of the monomers

(b): Bath temperature

(c): Intrinsic viscosity in dimethoxy ethane at 30 ± 1^0C

(d): Based on GPC

In this work we have not attempt to make an optimization for preparing polyesters with predetermined molecular weights.

Since esterification of the free hydroxy group with the carboxyl group is less favor at 120^0C the polymerization must take place via ring opening of the oxirane function at this temperature. As a result formation of linear polyester becomes predominant. Although it is difficult to assign a linear structure based on the NMR spectra, linearity seems to be more likely. In such case epoxy and carboxyl groups must retain at the chain ends after the reaction. Indeed prolonged heating of the viscous polymer solutions causes to rise in the viscosities, which indicates presence of the reactive groups at the chain ends. For instance heating of a poyester sample solution

for additional 1 hour at 120^0 results in rises of its molecular weight from Mn: 6200 to 13200.This can be ascribed to chain extension of the polyester by continued reaction of the epoxy groups at the chain ends. Unfortunately we were not able to a quantitative determination of the terminal oxirane groups by pyridinium chloride method. However this observation supports structure of the polyester depicted in Scheme 1.

Since the reaction in fast enough in this study we have not dealt with kinetics of the polyesterification.

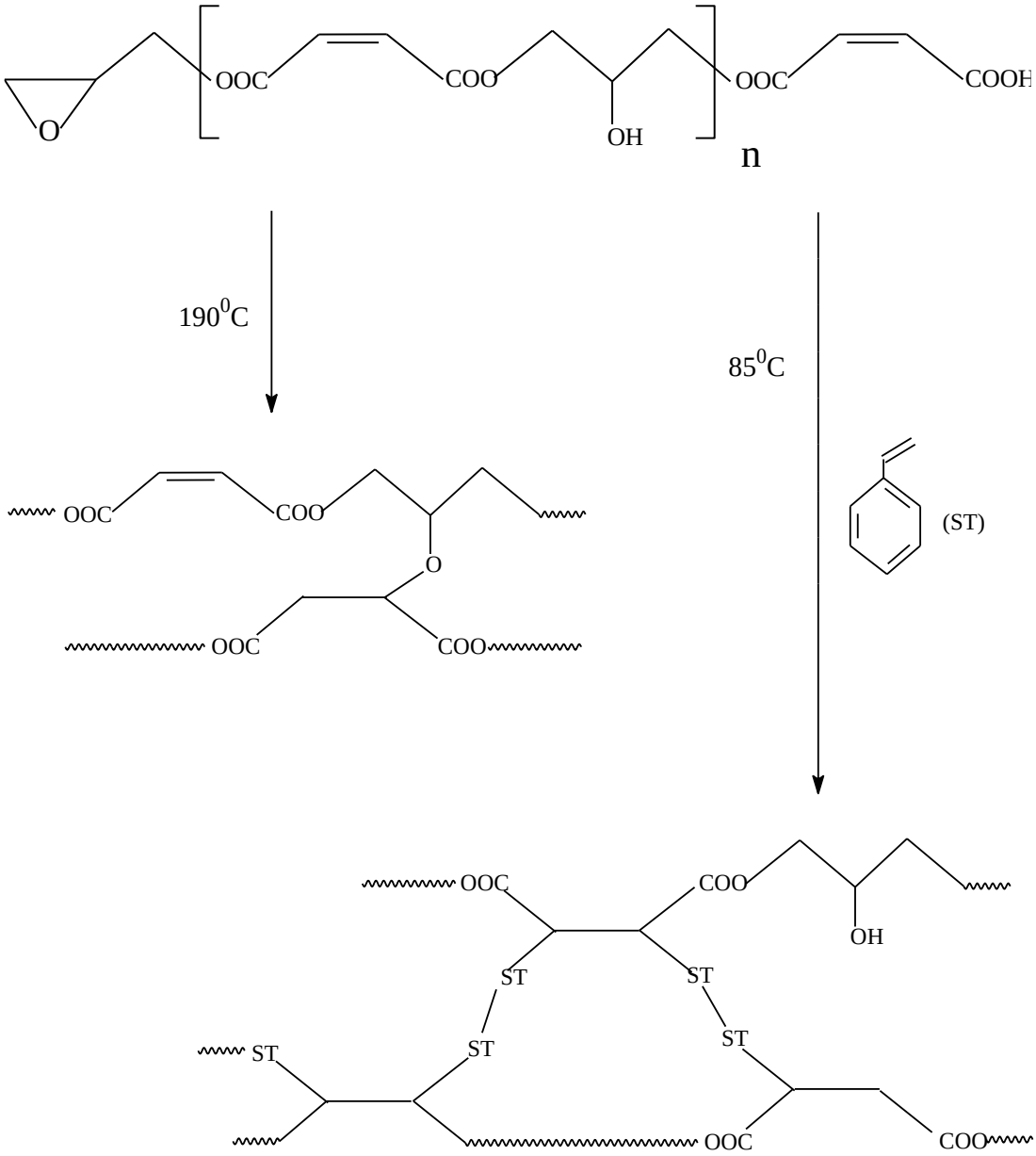
Overall result reveals that soluble polyesters can be prepared by controlled reaction in dimetoxyethane. The resulting polyester with one hydroxyl group in each repeating units is highly adhesive for various substrates such as metals and wooden goods and useful for post curing. Apparently OH groups involving provide adhesiveness to the product.

4.3 Crosslinking

Crosslinking of the polyester can be achieved either by thermal curing or cross-linking copolymerization with styrene monomer. Hard and insoluble material is obtained in each case. Optimum cure temperature for cross-linking of the polyester can be predicted from the DSC curve. The first two-step sharp exotherms of maleic anhdride-glycidol mixture are absent in DSC trace of the soluble polyester (solvent-free) (fig 1b). This fact is another evidence for the two-step mechanism. In DSC graph of the polyester a broad endotherm in 180-220^0C and an intense exothermic band centered at 350^0C can be ascribed to self- cross-linking and decompositions respectively. In the case for the maleic anhydride-glycidol mixture the endothermic peak is not clear and slight depletion in this range can not be ascribed to an endothermic peak, most probably due to a fast scan rate (10^0C/min) of temperature in comparison to the reaction rate at the second step.

Based on these considerations we have tested self-curing ability of the polyester by thermal curing at 190^0C for different time intervals. Efficiency of the curing was followed by inspection of soluble portions of the cured samples in acetone. There was no mass change of the samples cured for over three hours, as it has been represented in fig.5. Here, thermal-cross-linking must be due to addition of hydroxy

groups to the maleic double bonds to form ether linkages. This result is in accordance with reports in earlier literatures (7). C-O stretching vibration associated with the ether linkage is clearly observed at 1080 cm^{-1} in the IR spectra of the cured samples. As a result this polymer is self-cross-linkable material, which would be beneficial for various applications.



Scheme 2: Polyester networks by thermal curing and cross-linking copolymerization with styrene

Moreover, copolymerization with styrene is also efficient way of cross-linking. However pure polyester is not miscible with styrene. Addition of small amount THF gives homogenous mixtures. The mixture with two equivalents of styrene undergoes

cross-linking in about 35min when heated with benzoyl peroxide at 85 ^{0}C. In this work we have not studied details of the curing with styrene. Obviously, the styrene-based curing procedures are also applicable for this polyester.

In conclusion, soluble polyester with pendant hydroxyl group can be prepared by controlled heating of maleic anhydride glycidol mixture in dimetoxyethane as solvent. Without solvent the reaction yields cross-linked products. Hardening of the soluble can be achieved by cross-linking copolymerization with styrene. The soluble polyester is adhesive for metals and cellulose based materials, because of the hydroxyl functions involving. Having those peculiarities the soluble polyester presented seems to be especially suitable for spray coating applications. Further studies devoted to coating are under consideration.

5. CONCLUSION AND RECOMMENDATION

In this study soluble maleic acids polyesters possessing hydroxyl group in each repeating unit have been prepared starting from maleic anhydride and glycidol the difficulty in this reaction is that glycidol itself is a potential trihydroxy compound which may lead crosslinking when interacted with dicarboxylic acids.

Indeed when maleic anhydride is reacted with glycidol , without solvent, an insoluble cross-linked polyester is resulting product. In this work the crosslinking possibility has been avoided by controlled reaction in dimetoxyethane solvent. By this way it has been observed that soluble maleate polyesters with modorate molecular weight can be attained.The advantages of this reaction is that the process does not need to remove as in case of common polyester synthesis due to this fact the polyester formation takes only a few hours. The viscous polymer obtained is self curable. This makes it superior to common unsaturated polyester because general approach for cross-linking of unsaturated polyester is copolymerization with an additinal vinyl monomer such as styrene whereas this material presented can be hardened effectively by heating of the polyester film at 190^0C for three hourts.Aftercuring the material does not lose its caracteristic luster.

- Owing to these pecularities new soluble polyester presented here is a promising material for various application such as coating etc.
- Moreover the material can also be a potential candidate to prepare fast speed printing formulations due to its compatibility with the same inorganic colorants or pigments.
- Utility of this material in coating applications will be subjected in further studies.

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APPENDIXES

APPENDIX 1 DSC traces of maleic anhydride-glycidol mixture, (heating rate, 10^0C/ min., under N_2 atmosphere)

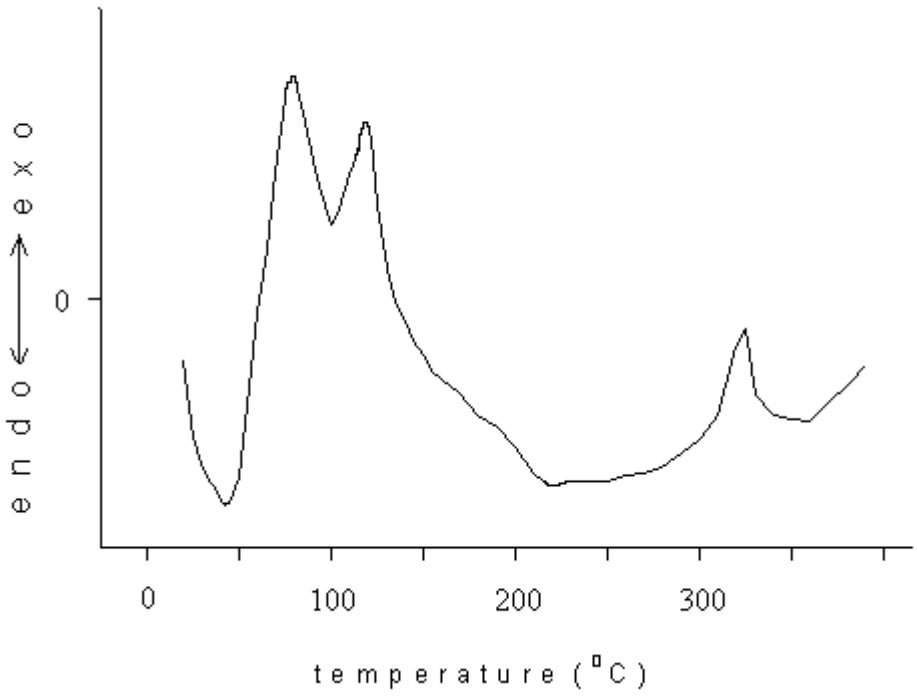

Figure 4.1

APPENDIX 2 ^{1}H-NMR spectra of monoglycidyl maleate(a), the polyester obtained by heating of MA-GL mixtures at 120^{0}C for 45 min.(b), in acetone-d_6 with TMS as internal standart.

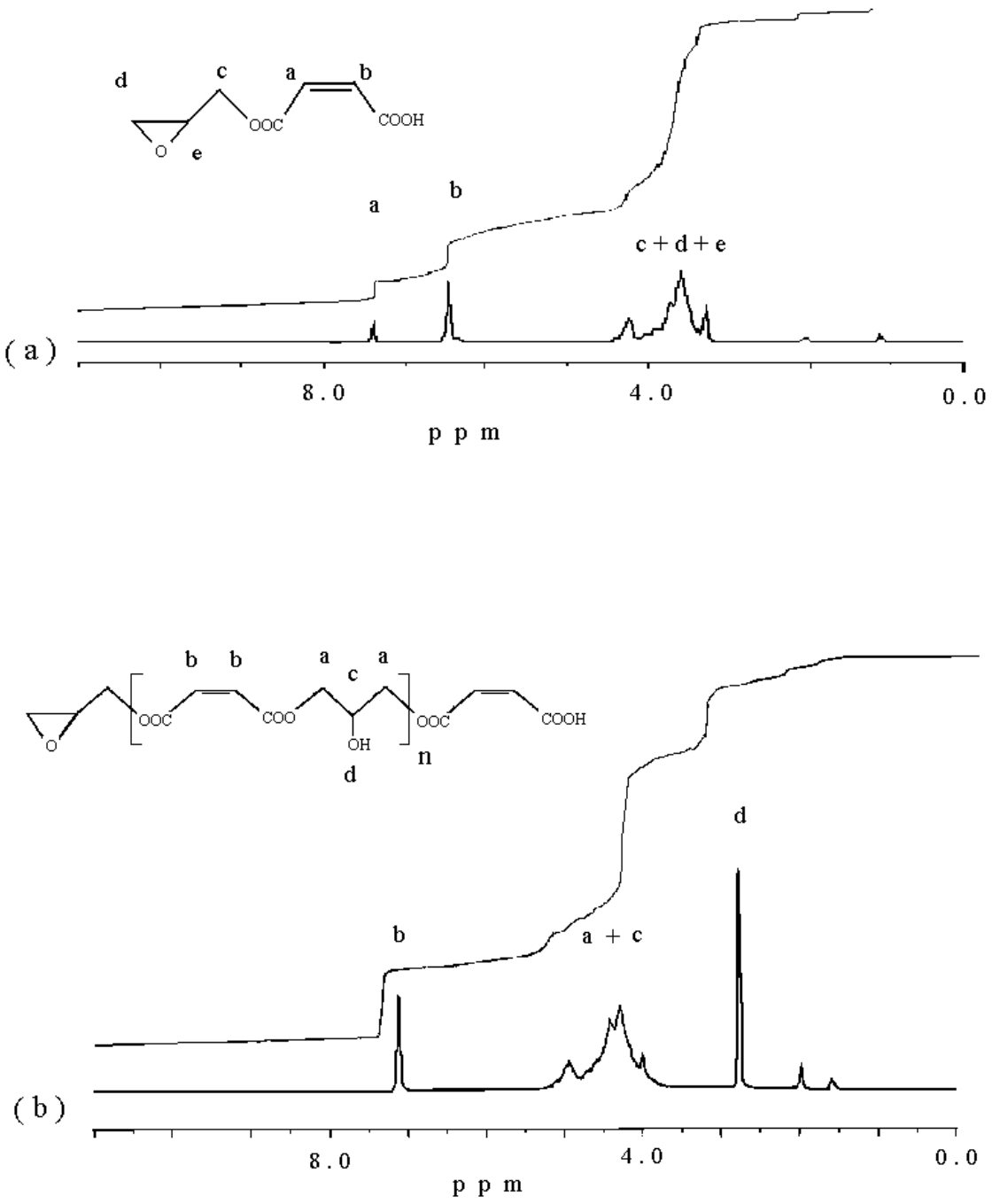

Figure 4.2

APPENDIX 3 GPC trace of the polyester (sample 4) in THF as solvent (Flow rate 0.3 mL/ min.) (see table 2.1)

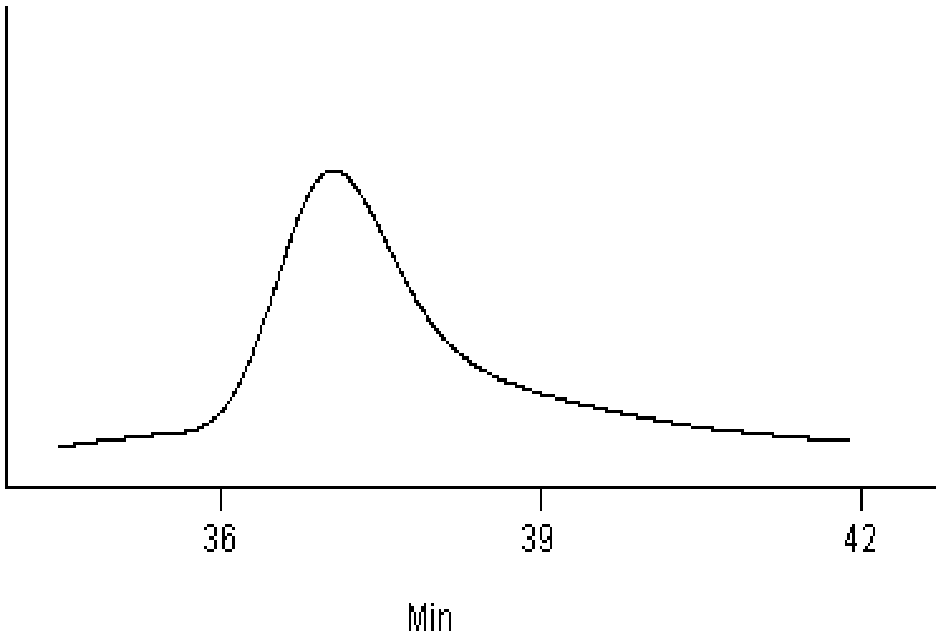

Figure 4.3

APPENDIX 4 Percentage soluble fractions of the polyesters cured at 190^0C

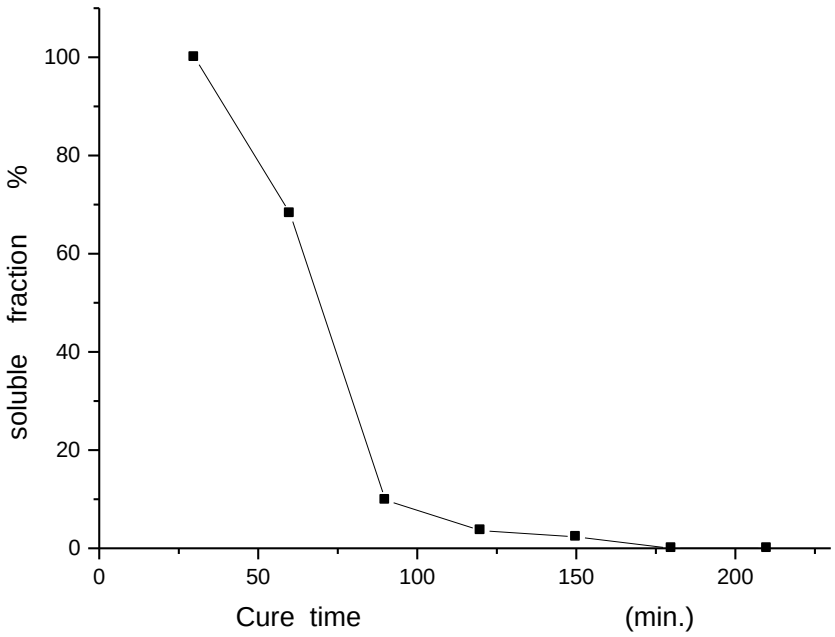

Figure 4.4

APPENDIX 5 FT-IR spectra of maleic anhydride with glycidol (sample 3 used in table 2.1)

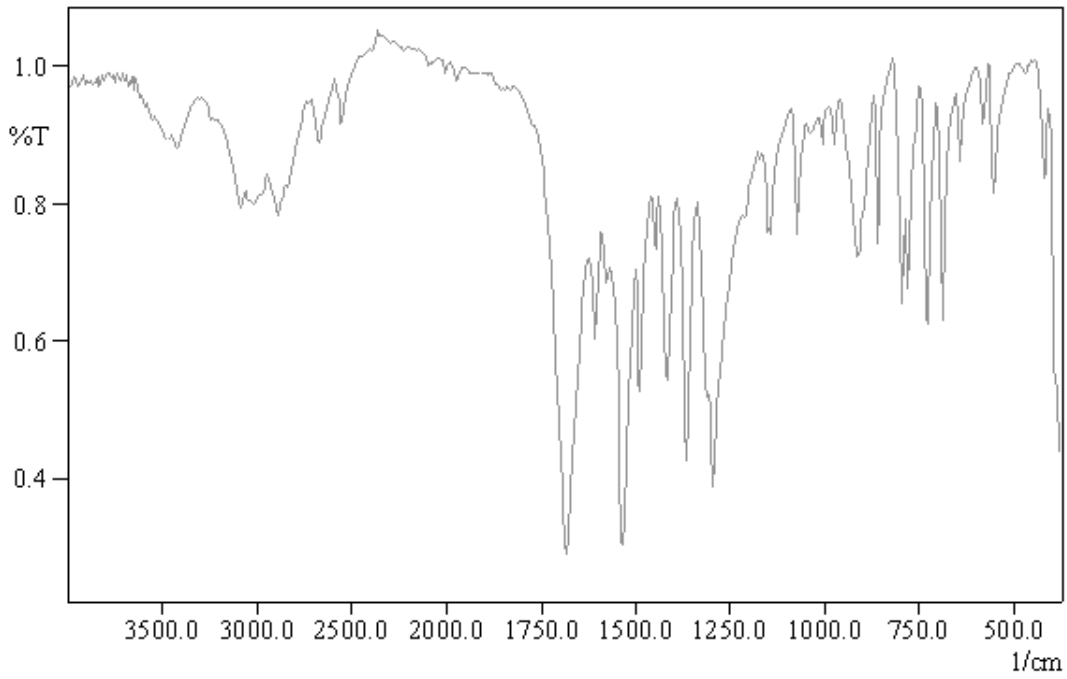

Figure 4. 5

AUTOBIOGRAPHY

He was born in 1977 in Çankırı.In 1996; he graduated from Fatih Sultan Mehmet High School and attempted to the Chemistry Department of Istanbul Technical University in 1996.

In 2001, he was accepted as a master student to Istanbul Technical University, Polymer Science and Technology Department of the Institute of Science and Technology.